TECHNOLOGY QUARTERLY

AND

PROCEEDINGS OF THE SOCIETY OF ARTS

Vol. XXI SEPTEMBER, 1908 No. 3

CONTRIBUTION FROM THE
SANITARY RESEARCH LABORATORY AND SEWAGE EXPERIMENT STATION
OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY

AN INVESTIGATION OF THE SANITARY CONDITION OF THE GOWANUS CANAL, BROOKLYN, NEW YORK

BY CHARLES F. BREITZKE

INTRODUCTION

THE following is an abstract of a part of the thesis submitted in May, 1906, by Norman P. Gerhard and the writer, at that time candidates for the Degree of Bachelor of Science at the Massachusetts Institute of Technology.

The object in view in the preparation of the original thesis on file in the Engineering Library at the Institute was to investigate the condition of the Gowanus Canal, Brooklyn, New York, and to suggest a plan for remedying the nuisance. The sanitary investigation was made by the writer. The discussion of the methods which might be applied to remedy the conditions was written by N. P. Gerhard. In view of the fact that the problem has also been considered by the Brooklyn engineers and that a flushing tunnel is now under construction, it was thought best in the publication of this abstract to omit N. P. Gerhard's part of this study.

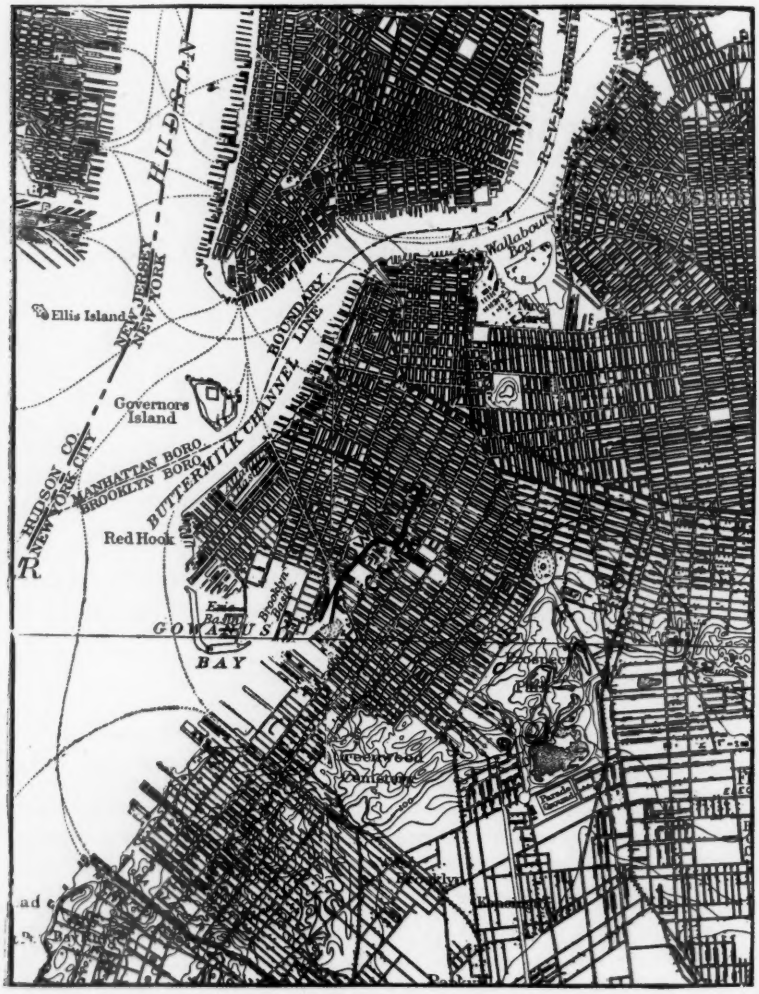

FIG. 1.— MAP OF A PORTION OF NEW YORK HARBOR SHOWING THE LOCATION OF THE GOWANUS CANAL

GENERAL DESCRIPTION

Location. — The Gowanus Canal is located in the western part of the Borough of Brooklyn, City of New York, midway between Prospect

Park and Upper New York Bay. The canal is closed at its upper end and opens at the lower end into Gowanus Bay, a part of New York Harbor. Its position is best seen by a study of the appended United States Geological Survey map (Fig. 1).

Construction and Data. — Originally this portion of Brooklyn contained a stream known as Gowanus Creek. Its shores were everywhere surrounded by great salt marshes formed by the combined action of the tide and the wash from the surrounding upland. This inlet was then navigable at all stages of the tide. Since that time the marshes have been entirely filled in, mainly from gravel knolls which were cut

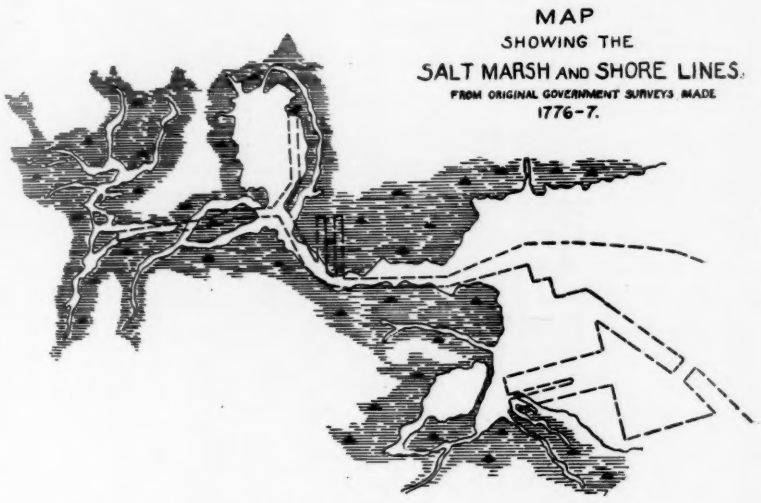

FIG. 2.

down in the western part of the city. The original shore line in 1776 and the present outline of the canal are shown on the accompanying map (Fig. 2). A glance at the topographical map shows that the land slopes down towards the canal on the north, east, and west; while on the south it is flat, this being made land. For the length of a block on either side of the canal the ground is practically level.

The act authorizing the construction of the canal was passed in 1849. The original cost of construction was $452,131, and this was assessed on the portion of the city benefited. The lateral basins provided for were to be built by private enterprise. The date of completion was about 1860.

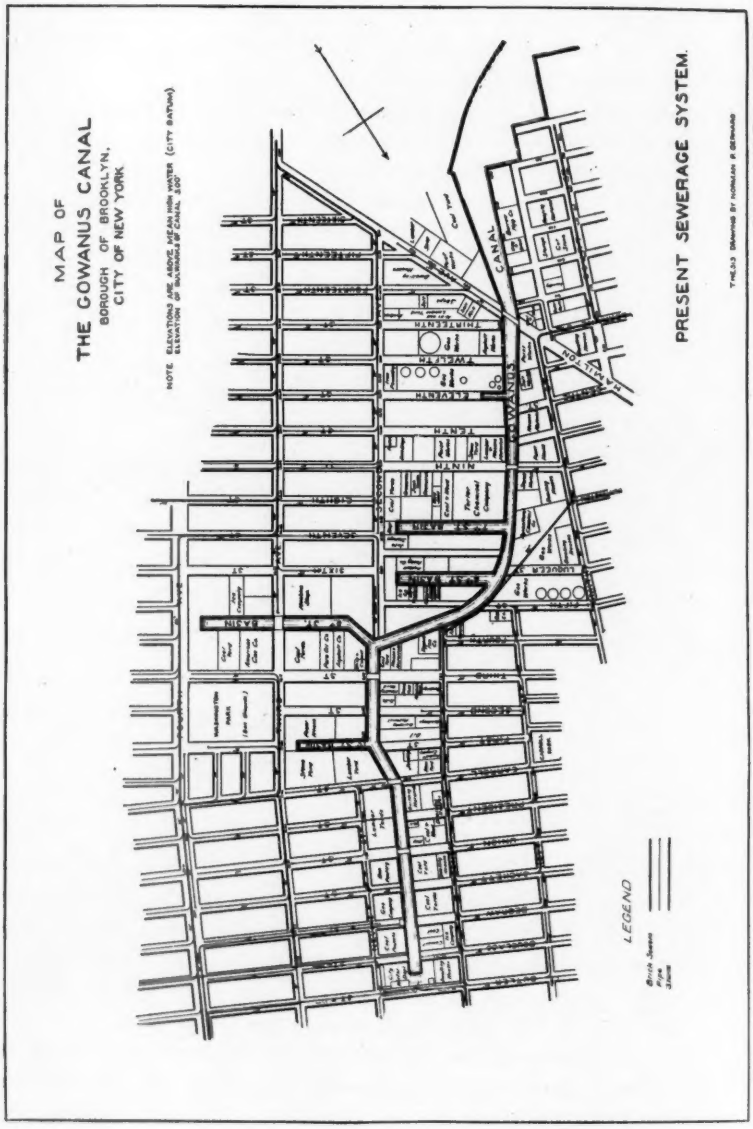
MAP OF
THE GOWANUS CANAL
BOROUGH OF BROOKLYN,
CITY OF NEW YORK
PRESENT SEWERAGE SYSTEM.
SCALE: 1200 FEET = ONE INCH
LEGEND
GOWANUS CANAL
BASIN
THIRTEENTH
TWELFTH
ELEVENTH
TENTH
NINTH
SEVENTH
SIXTH
HAMILTON AVE.
LUQUER ST.
CARROLL ST.
DEGRAW ST.
BAYARD ST.
WILLIAMSBURG

FIG. 3

The canal (Fig. 3) was constructed with two objects in view. One was to drain this section of the city, including an area of about 1,700 acres, chiefly marshes, and to make it fit for agricultural use and building purposes. The other object was to make a navigable waterway for all river and coasting craft, such as sloops and schooners of light draft, towboats, and barges.

The length of the main canal is about 6,575 feet, and the lateral basins are approximately 3,600 feet in length. The total length is, therefore, about 10,175 feet, or somewhat less than two miles. The legal width of the canal is 100 feet. Its average depth is 10 feet below mean low water, but the variations in depth are considerable. At the head it is about 5 feet deep and it grows gradually deeper as Hamilton Avenue is approached. The total capacity of the canal at mean low water is approximately 10,000,000 cubic feet.

Nature of the Locality. — The locality is chiefly a commercial one and consists largely of factories and yards. Certain portions toward the lower end and on the eastern side are not yet built up, and there remain numerous empty lots. The factories and yards extend the entire length of the canal and for the distance of a block on either side. These include gas works, factories, chemical works, ice plants, salt works, oil refineries, asphalt and paving material plants, building material yards, coal and wood yards, power houses, machine shops and foundries, storage warehouses, junk yards, and city dumps.

Immediately adjoining this business section on either side of the canal is a thickly populated tenement district. Gradually, as the distance from the canal increases, more and more houses are found, and the better residence sections are within five blocks on either side.

The photographs accompanying this article (Figs. 4 to 7) give a general idea of the nature of the locality.

Value of the Property. — The assessed value of the land fronting the canal is $3,315,000. The canal enables the abutters easily to obtain supplies of coal, brick, lumber, oil, etc., from schooners and canal boats towed up the canal by tugs. An examination of records on the amount of traffic on the Gowanus Canal showed that during a recent year 26,680 vessels passed Hamilton Avenue, an average of eighty-seven per day. At Ninth Street, Third Street, and Union Street, the average per day was eighty, forty-eight, and twenty-four vessels, respectively. There is no railroad in this part of the city, and the canal is therefore a great convenience.

FIG. 4.—FIFTH STREET LATERAL BASIN

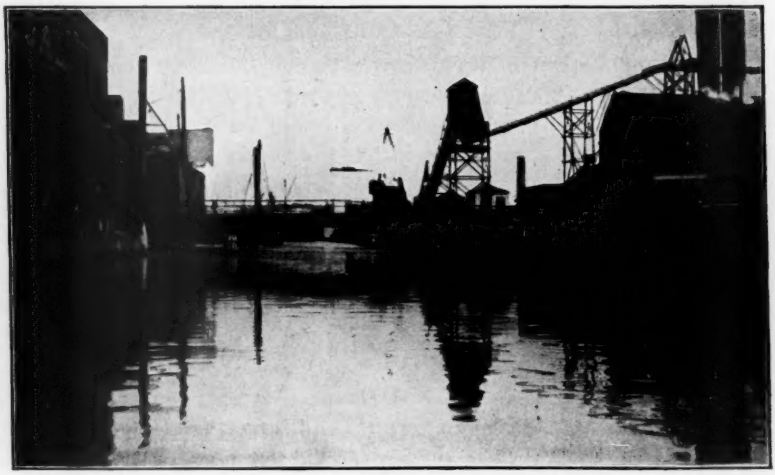

FIG. 5.—CARROLL STREET BRIDGE

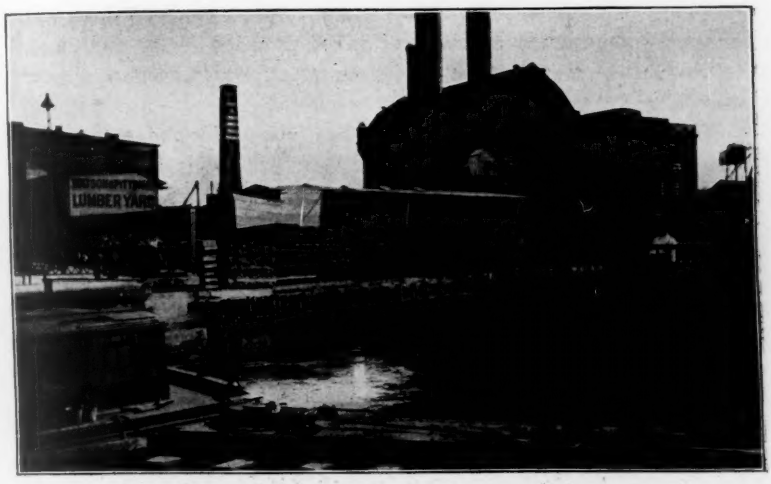

FIG. 6.—VIEW LOOKING SOUTH FROM UNION STREET BRIDGE

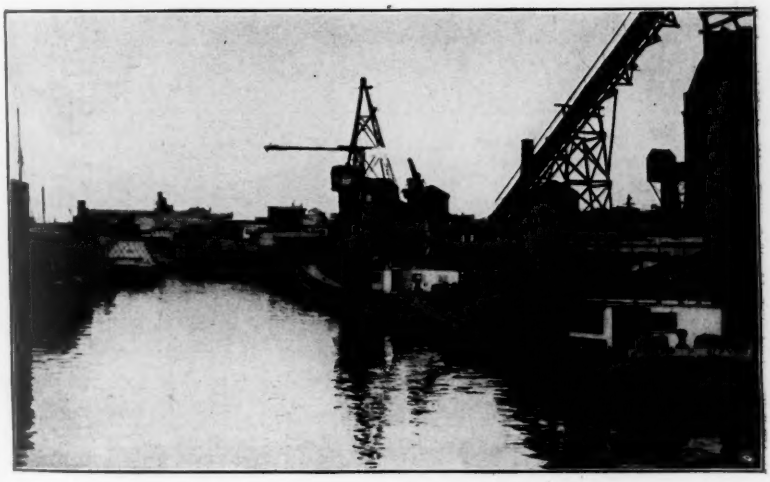

FIG. 7.—VIEW LOOKING NORTH FROM CARROLL STREET BRIDGE

Tributary Sewers.— With the single exception of Chicago, Brooklyn was the first city in this country to undertake a complete system of sewerage. Therefore when the sewerage system was planned the designing engineer was dependent upon English experience for data in regard to the amount of sewage to be provided for, as well as for the amount of rainfall from any given storm which reaches a sewer within a given time.

The sizes of sewers were determined mainly by the extremes of rainfall, the household sewage being a very small item in comparison. The sewerage was installed in the early sixties. Brooklyn grew very

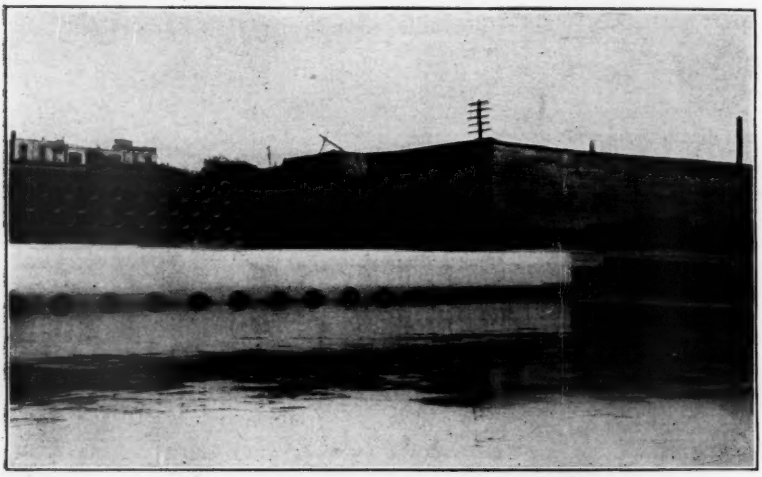

FIG. 8.— OUTLET OF SILT BASIN AT HEAD OF CANAL

rapidly. Consequently by 1888 the sewers became too small, and the legislature of that year passed an act permitting the discharge of storm water sewers into the Gowanus Canal. In 1892 a 15-foot main relief sewer, which intercepts all the storm water in the mains draining that portion of Brooklyn lying south of Greene Avenue, was brought down to the head of the Gowanus Canal, at Butler Street (Fig. 8), and completed. Nothing but storm water was intended to enter this relief sewer, but, whether by accident or design, it is now flowing during dry weather and is discharging sewage into the canal.

In addition, the following storm overflows have also been con-

structed: 78-inch overflow from Nevins Street at the head of the canal; 60-inch overflow from Bond Street at the head of the canal; 42-inch storm sewer on Douglass Street; 90-inch storm sewer on Degraw Street discharging through a silt basin; 78-inch overflow from Third Avenue main sewer discharging at Second Avenue; 72-inch overflow from Bond Street main sewer discharging at foot of Bond Street.

All of these sewers bring down more or less diluted sewage and street washings during times of storm. The contents of the canal are of the vilest sort. Practically all the industrial plants on the streets adjoining the canal discharge directly into it. The following sanitary sewers empty into the canal: 18-inch sewer on Sackett Street; 18-inch sewer on President Street; 12-inch sewer on Carroll Street; 12-inch sewer on Ninth Street; 12-inch sewer on Hamilton Avenue; 48-inch sewer on Grinnell Street.

With the above exceptions, the streets which terminate at the canal have been left unsewered. The reason given is that there was not sufficient grade to drain the sewers into the mains in the streets running parallel and on either side of the canal.

Current and Deposits.—The canal is always filling up and a constant expenditure of money is required for dredging. The importance of this factor is shown by the following figures on the cost of dredging taken from various reports:

1875	550 feet west and 500 feet east of Bond Street	$2,500.00
	At Third Street bridge	250.00
1876	No dredging.	
1877	Gowanus Canal	325.00
1878	Gowanus Canal at various bridges	1,995.00
	Gowanus Canal at Sackett Street	130.00
1879	Gowanus Canal at various bridges	1,995.00
	Gowanus Canal at various localities	513.00
1880	Gowanus Canal	1,019.70
1881–1884	No records.	
1885	From Douglass Street (7 feet at low water) to Hamilton Avenue (12 feet at low water)	16,450.00
1886–1893	No records.	
1894	From Butler Street to Union Street	2,980.00
1895	Entire length and width	7,527.00
	Soundings	37.75
1896	Dredging Gowanus Canal	990.00

1897–1901	No reports available.	
1902	Dredging	$5,051.00
	Engineering expenses	106.25
	Inspection	222.50
	Total of all available records . . .	$42,092.20

At present barges at the upper end of the canal are aground at low tide. The depth of the canal is now inadequate for the passage of fireboats.

The mere rise and fall of the tide have apparently no purifying effect whatever, and do not prevent the filling up of the canal with the heavier portions of the sewage. Only after heavy rainstorms, when a large amount of water is discharged from the storm sewers, is there any current noticeable.

Appearance and Odors. — The surface of the water in the canal is covered with a layer of oil, coal dust, and scum. Gases are constantly seen bubbling up through the water, especially at the upper end of the canal. In the summer time the stench at the canal is unbearable, and it is noticed at all times a block away. On certain days not only the immediate locality, but also large sections of the city on the north, west, and east, according to the direction of the wind, are seriously affected. The section on the west was formerly a handsome residence district, but in part owing to this annoyance property has steadily declined in value in the past twenty-five years.

Investigation of the Sanitary Conditions

This investigation was undertaken to learn as much as practicable within a limited time regarding the character of the water now filling the Gowanus Canal and the nature of the pollution now entering it.

In a general way all this work has been undertaken to answer as clearly as possible the following questions:

1. Are all the odors due to the canal or are they due to manufacturing plants along the sides?

2. What is the character of the water which now fills the canal? What is the amount of organic matter present and the amount of oxygen necessary to destroy it? Are there any chemical wastes which inhibit the reduction or oxidation of putrescible substances? What is the amount of those substances which appear to be indifferent to chem-

ical changes, but which silt up the canal? How does the canal water compare with unpolluted sea water? How does it compare with the water in that part of the harbor adjoining its outlet?

3. What is the character of the entering pollution from the factories? Which is the larger factor in bringing about pollution, industrial wastes or sewage?

4. Do the ebb and flow of the tide renew the water in the canal, or does much of this water flow back and forth?

5. Is the water continually active in digesting or oxidizing and capable of rendering innocuous the pollution that comes into it?

6. What is the proportion of sewage, fresh water, and salt water in the canal; that is, what is the sewage density or the quantity of sewage per cubic foot of water?

7. What quantity of East River water would be required to dilute sufficiently the daily discharge? What quantity will be required to flush out the present contents of the canal if dredging is first resorted to?

This report will be divided into five parts:

1. The sanitary inspection.
2. Chemical and bacteriological analyses, with their interpretation.
3. Summary of existing conditions.
4. Recommendations, with calculation of the water to be pumped.
5. Summary and conclusions.

The Sanitary Inspection

As careful an inspection as the time would permit was made, especial attention being paid to the incoming sewers and resulting conditions. The canal in its present state is exceedingly obnoxious, the stench even in the winter time being very disagreeable. The water is black, warm, and foul. No fish have been caught in the canal for many years. There is practically no current. The appearance of the surface and bulwarks is disgusting, especially near the sewer outlets.

The surface of the canal is covered with scum. In the upper portion (Fig. 9) this is characteristic of domestic sewage, such as grease and slime, partially disintegrated human fæces, and other organic matter. The lower portion of the canal from the Bond Street sewer outlet to Gowanus Bay is covered with unsightly patches of floating rubbish

which have been accumulated by the action of the tugboats, wind, and tide. These patches consist largely of brown and yellow oily substances, which spread out in thick layers on the water surface and seem to gather up all the other floating *débris*, such as waste paper, fecal matter, melon rinds, banana skins, kitchen refuse, tin cans, broken boxes, coal dust, and other matter.

The water throughout the canal is exceedingly turbid, especially at the upper end. The turbidity is so great that the water is of a light gray color. The color becomes darker, however, and the turbidity

FIG. 9.—VIEW LOOKING NORTH FROM UNION STREET BRIDGE SHOWING LAYER OF SCUM IN THE FOREGROUND

less as the outlet is neared. In no place in the canal is it possible to see the oar blades when in a rowboat.

Practically all the plants along the canal discharge directly into it, but the amount of sewage from these is small when compared with that contributed by the city sewers. Not only is the discharge of the sewers greater than that of the factories, but its amount and its offensive character are shown by the bad condition of that part of the canal into which it discharges. These sewers have all been named in the first part of this report. All the so-called "storm sewers" in dry weather discharge concentrated sewage, as the chemical analyses will show. The chief

offender, however, is the 15-foot relief sewer at the head of the canal. During the quieter hours of the day the depth of the dry weather flow in this sewer is about 6 inches. This is continually bringing down waste paper, hair, and other sewage stuff. White scum covers the water surface in front of its outlet. Slaughterhouses drain into this sewer, for at times large quantities of blood are discharged. On wash days suds are in abundance.

A large silt basin was provided at the head of the canal to settle out the solid matter and detritus carried down in the storm sewers during heavy rains. A photograph of the silt basin is shown in Figure 8. The settling basin, however, intercepts only the coarse, heavy material. The finer material passes through and silts up the canal. In October the canal was dredged from Union Street to the head end. By February the deposit in front of the outlets filled up this section of the canal to approximately 5 feet below mean low water. In April the top of this bank was only about 3 feet below. The conditions are such that at low tide all the canal boats are aground in this portion of the canal.

The continuous discharge of the Bond Street sewer was easily detected by means of the brown and yellow oily substance already referred to. This sewer has two 36-inch outlets.

Among the more conspicuous of the private sewers are those of the gas works, which continually discharge a yellow-brown liquor. There are several of these gas plants. Their discharge outlets are from 8 inches to 12 inches in diameter and discharge full. It is to this, doubtless, that the tarry incrustation of the posts and bulwarks of the canal is due.

Much hot water is discharged into the canal. In cold weather this causes a heavy fog to hang over it. The large amount of vapor given off and the constant bubbling up of gases make the canal look boiling hot. In February the temperature of the water was 65° F. at the head of the canal. This gradually became higher on going down the canal, until at Carroll Street, where a large power plant is located, it became 70°. From here to the First Street basin the temperature rapidly became higher until 90° F. was reached. On going down the canal this soon dropped again to 70° F. and then gradually diminished, until at the entrance to the bay it became 44° F. In April the temperatures were a little higher, but varied in the same way.

The semi-liquid layer of sludge at the bottom requires merely a

slight rise of temperature to cause the development of gases, which bubble up in practically the whole length of the canal. At the head end the bubbling is violent. Black solid matter arises to the surface, and discharging its burden of gas again disappears from view. The white scum at the head end is blackened and the smell is rank, becoming unbearable when the water is stirred up by the tugboats.

To sum up: The canal is an open sewer, or rather, in its present state, practically a septic tank. There is almost no current and the tide appears to exert no flushing effect whatever. Of the plants along the canal, the gas works are doubtless the chief offenders. The trouble, however, is due largely to the discharge from the city sewers, which discharging into a body of quiet water cause heavy deposits to be formed. The canal water being stagnant and devoid of oxygen, the deposits putrefy and are the seat of the nuisance. These conclusions are borne out by the chemical and bacteriological analyses.

Chemical and Bacteriological Analyses

Before taking up the regular analytical work, it was thought best to ascertain from a few preliminary samples from various portions of the canal the character of the water to be analyzed.

Two of these samples, one taken at the Union Street bridge near the head of the canal, and the other at the Ninth Street bridge near the lower end, gave interesting results. The first was strongly indicative of sewage, the other of industrial wastes. Tests were made for acidity. The first was found to be neutral to litmus, acid to phenolphthalein, and alkaline to methyl orange. The other, although neutral to litmus, was acid to both phenolphthalein and methyl orange. Both were decidedly turbid and had much matter in suspension. The behavior on evaporation on the steam bath and on ignition also deserves attention. The first blackened readily on ignition and gave off a strong sewage odor. The second on the bath gave off an acetic acid odor; on ignition the solid matter decrepitated, and the odor was at first leathery, then like fertilizer, and finally very offensive. The substance burned with great difficulty, indicating vegetable carbon. Both samples contained a large amount of chlorine and sulphates, the second, however, in much greater proportions than the first.

Pollution by the gas plants was particularly evident, both from the odor of the water and from the color and behavior of the precipitate formed on nesslerization. This, instead of being of the reddish color

characteristic of ammonia, was a heavy, curdy precipitate, canary yellow in color, the reaction indicating amines.

It was decided in the regular series of analyses to make the following six tests chemically: oxygen consumed, total organic nitrogen, free ammonia, dissolved oxygen, turbidity, and chlorine. From ratios of these six in sea water and sewage an attempt has been made to determine the degree of pollution of the canal.

Method of Taking Samples. — In obtaining samples care was taken to choose representative points along the canal and to guard against accidental or abnormal conditions. The samples were taken from a rowboat at different depths and at different points in a cross-section of the canal. This was done by letting up and down a large bottle with a double perforated stopper while rowing across the canal. The contents of the bottle were then emptied into a pail and a liter bottle was filled from the mixture. This method gave a sample which was fairly representative of the cross-section of the canal from which it was taken.

As soon as the samples for the entire canal were obtained they were immediately taken to the Mount Prospect Laboratory, which was within twenty minutes' ride from the canal.

Methods of Chemical and Physical Analysis. — With the exception of the test for turbidity, the methods of chemical and physical analysis were those recommended by the Committee on Standard Methods of Water Analysis. The oxygen consumed was determined by the five-minute-boil method, the nitrogen content by the Kjeldahl Process, and the free ammonia by direct nesslerization. The turbidity was determined by means of the Jackson turbidimeter. The observation was made by pouring the sample of water into the tube until the image of the candle disappeared. The turbidity was then read from a graduation on the side of the tube. This graduation corresponded to the turbidity produced in distilled water by a certain number of parts per million of silica standard.

Methods of Bacteriological Analysis. — The media used for this work were standard media, made according to the procedure established by the Committee on Standard Methods of the American Public Health Association. The determinations were made for total count per cubic centimeter by plating on gelatin at 20° C., body temperature count on litmus lactose agar at 37° C., and tests on gas production, the latter being the only tests for *B. coli* considered necessary. In plating, two dilutions, one to 1,000 and one to 10,000, respectively, were made.

In the first series of analyses, use was made of the method of direct

inoculation of 1 c.c. of the canal water into the Smith fermentation tube, but in a second series this method was abandoned in favor of Dr. Jackson's new bile media.[1]

Tests for Bacillus coli. — In the fermentation tubes 25 per cent. to 70 per cent. gas was considered indicative of the colon bacillus, and a positive record was made if the other tests were favorable, *i. e.*, if the proportion of CO_2 fell within the right limit. This limit was from 25 per cent. to 40 per cent. absorption by caustic.

First Series of Analyses

Dissolved Oxygen. — Examinations of the water for dissolved oxygen were carried on simultaneously with the sanitary inspection. About thirty samples were taken at intervals along the canal from the head end to Hamilton Avenue, and, with the few following exceptions, negative results were obtained. Four surface samples also were taken from the East River, and the results of analysis are given in the second table below.

Gowanus Canal

No.	Place of collection.	Temperature.	c.c. oxygen per liter.	Per cent. saturation.
1	Entrance to power house basin, 4 P.M.	80° F.	1.14	20.2
2	East pier, Third Street bridge, 4 P.M.	70° F.	0.58	9.3
3	Entrance power house basin 9 A.M. next day	90° F.	1.54	30.4
4	Just below basin	90° F.	1.05	20.7
5	Above Third Street bridge	70° F.	1.03	16.5
6	Below Third Street bridge	70° F.	1.01	16.2
7	20 feet below Third Street bridge	70° F.	0.73	11.7
8	75 feet below Third Street bridge	70° F.	0.30	4.8
9	100 feet below Third Street bridge	70° F.	0.00	0.0

East River

No.	Place of collection.	Temperature.	c.c. oxygen per liter.	Per cent. saturation.
1	Buttermilk Channel, 200 feet from Brooklyn side	35° F.	7.50	77.4
2	Mid-stream opposite Governor's Island	30° F.	7.58	74.5
3	Return trip, same as 2	30° F.	7.95	78.0
4	Buttermilk Channel, 75 feet from Brooklyn side	34° F.	7.90	80.5

[1] For description, see Biological Studies by the Pupils of William Thompson Sedgwick, Boston, 1906, pp. 292–299.

The other results of the first series are shown in tabulated form in Table I.

Analysis of the Sludge.— Samples of the sludge which appeared to form a semi-liquid layer on the bottom were analyzed for total solids, oxygen consumed, and total organic nitrogen Inasmuch as the method of taking samples was crude and allowed some water to mix with the sludge, the density was changed. The results are therefore expressed in ratios for comparison.

Location of sample.	Oxygen consumed : total nitrogen.	C + N : total solids.
Head of canal	16.2	1 : 1.9
150 feet below head	13.0	1 : 2.0
300 feet below head	9.8	1 : 2.2
Opposite Degraw Street	11.0	1 : 2.1
Entrance First Street basin	10.3	1 : 3.3
Entrance Fifth Street basin	7.0	1 : 3.1
Opposite Bond Street	13.0	1 : 3.5

Experiments were made on the temperature necessary to develop gases from the sludge. Ten c.c. of the various samples were diluted to about 60 c.c. and placed on ice. After standing on the ice for several hours, all the foul air possible was exhausted and replaced by fresh air. The bottles were then set back into the ice chest and allowed to remain there over night. The temperature of the ice chamber was 2° C. At this temperature no sewage odor was noticeable. The samples were then allowed to stand in the room, and their condition was noted from time to time. No. 1 became offensive at 12° C.; Nos. 2, 3, and 4 at 12.5° to 13° C. Sample No. 5 contained a quantity of tarry matter and required a temperature of 14° C. to become offensive. The samples were then slowly warmed. At 20° C. the odor was very strong. At 23° C. the stench became vile and unbearable, especially in the first three samples.

A sample of the incrusting substance on the bulwarks was also taken. On analysis this was found to be a tarry waste product of the gas works.

Second Series of Analyses

The first series of analyses was made in February, 1906. The second was carried out in April. This series included a sample of

TABLE I. — SHOWING ANALYSIS OF SAMPLES TAKEN FROM THE GOWANUS CANAL, FEBRUARY 3, 1906

CHEMICAL ANALYSIS (Parts per Million)

No.	Place of collection.	Temperature.	Turbidity. (Parts per million of silica.)	NITROGEN AS		Chlorine.	Oxygen consumed.	Number of bacteria per c.c., 48 hours at 20° C.	B. COLI
				Total organic nitrogen.	Free ammonia.				In 1 c.c.
1	Head of canal	. .	420	50.4	17.0	300	95.3	3,220,000	+
2	Just below Degraw Street	. .	265	44.0	17.0	1,400	64.0	1,440,000	+
3	Just below Carroll Street	. .	100	12.2	7.0	4,000	46.4	252,000	+
4	Entrance First Street basin	90° F.	105	10.4	4.4	5,700	36.8	99,000	+
5	Entrance Fifth Street basin	. .	125	8.2	6.6	5,900	43.2	171,000	+
6	Opposite Bond Street	. .	95	10.4	4.4	6,400	28.8	168,000	+
7	In Sixth Street basin	. .	160	14.7	6.1	6,200	45.6	217,000	+
8	Entrance Eighth Street basin above tartar factory	. .	100	15.9	3.3	6,700	42.4	217,000	+
9	Below Ninth Street	65° F.	90	13.9	5.3	7,000	35.2	254,000	+
10	Below Hamilton Avenue	55° F.	110	4.8	4.8	7,450	56.8	90,000	+
11	Entrance to bay	44° F.	120	13.5	5.7	7,500	102.4	69,000	+

NOTE. — Samples were taken at time of flood tide.

sewage taken from a manhole at the corner of Nevins and Butler Streets, and fifteen samples taken from different portions of the canal. The sample from the manhole was taken on Saturday morning, April 14. The depth of flow in the sewer was 6 inches. The samples from the canal were not taken until Monday morning, April 16. A heavy rain fell on Saturday night and Sunday morning, and the canal water was well stirred up.

In this series samples were analyzed both filtered and unfiltered, and the test for total solids was added. In the latter the sodium chloride present rapidly took on moisture from the air, and for that reason the tests for total and dissolved solids are rough and therefore of not much importance. The results of the second series are given in tabulated form in Table II.

Tests for putrescibility of the sewage and the degree of dilution necessary were made by the methylene blue test. This was done by adding 1 c.c. of a 0.1 per cent. solution of methylene blue to a half pint of the different dilutions of the sewage with tap water. These tests showed a dilution of one part sewage to fifteen parts water to be necessary for a stable mixture.

Interpretation of the Results

Interpretation of Figures Obtained. — The tabulated results give evidence of the amount and nature of the pollution. Tables, however, show more when they are represented graphically. Therefore to aid in the interpretation the results obtained have been plotted. The construction of the diagrams needs no explanation. The curves are striking and interesting. With the exception of those for chlorine and total and dissolved solids, they all have a general downward tendency, which shows the effect of dilution with sea water. The curves for the first series are much smoother than those for the second, because the second series of samples was taken after the canal had been stirred up by a heavy rainfall. It will be interesting to examine the curves and to account for the variations which occur.

Total Organic Nitrogen. — In the first series (Fig. 10) this curve falls rapidly until Bond Street is reached. Here it again rises, reaching a maximum opposite the Tartar Chemical Company.

In the second series (Fig. 12) there is a general decrease. The curve drops rapidly at the entrance to the First Street basin. This is

TABLE II. — SHOWING ANALYSIS OF SAMPLES TAKEN FROM THE GOWANUS CANAL, APRIL 16, 1906

CHEMICAL ANALYSIS (Parts per Million)

No.	Place of collection.	Temperature.	Turbidity (parts per million of silica).	Nitrogen as: Organic nitrogen: In solution.	Nitrogen as: Organic nitrogen: In suspension.	Nitrogen as: Organic nitrogen: Total.	Nitrogen as: Free ammonia.	Total solids.	Suspended solids.	In solution.	Chlorine.	Oxygen Consumed: In solution.	Oxygen Consumed: In suspension.	Oxygen Consumed: Total.	Number of bacteria per c.c., 48 hours at 20° C.	B. Coli: In 0.1 c.c.	B. Coli: In 1 c.c.	B. Coli: In 10 c.c.
	Sewage taken from manhole, corner Nevins and Butler Streets, April 14, 1906, 9 A.M.	..	475	51.8	19.5	71.3	36.0	1,860	1,220	640	230	116.4	48.6	165.0	3,120,000	+	+	+
1	Head of canal	77°.0 F.	380	30.5	19.3	49.8	24.0	1,160	260	900	350	42.3	33.2	75.5	—	+	+	+
2	Opposite Sackett Street	77°.0 F.	320	17.8	25.7	43.5	11.0	3,580	320	3,260	1,010	48.6	37.4	86.0	1,680,000	+	+	+
3	Below Carroll Street	99°.5 F.	1,000	8.8	22.5	31.3	4.0	11,980	480	11,500	4,600	17.6	91.7	109.3	1,280,000	+	+	+
4	Entrance First Street basin	101°.3 F.	150	9.8	1.6	11.4	3.0	10,720	1,260	9,460	4,700	16.2	9.2	25.4	1,030,000	+	+	+
5	Above Third Street	91°.4 F.	400	5.3	12.8	18.1	4.3	12,380	620	11,760	4,600	17.6	67.8	85.4	685,000	+	+	+
6	Opposite Fifth Street basin	73°.4 F.	265	24.8	12.8	37.6	4.0	10,540	2,440	8,140	4,850	14.1	32.4	46.5	670,000	+	+	+
7	Below Bond Street	..	385	8.8	4.8	13.6	4.0	15,540	6,600	8,940	3,890	20.4	57.1	77.5	643,000	—	—	+
8	Opposite Sixth Street basin	..	155	7.8	1.0	8.8	4.0	7,100	380	6,720	3,100	16.9	7.1	24.0	360,000	+	—	+
9	Above Seventh Street basin	55°.4 F.	160	8.3	2.6	10.9	3.5	11,300	1,820	9,480	4,100	12.7	8.5	21.2	228,000	+	+	+
10	Below Seventh Street basin	..	175	19.9	6.4	26.3	2.5	9,500	180	9,320	4,200	12.7	7.0	19.7	223,000	+	+	+
11	Below Ninth Street	..	290[1]	6.8	3.2	10.0	6.0	9,480	780	8,700	4,480	14.8	4.9	19.7	219,000	+	+	+
12	Above Eleventh Street basin	..	90	7.1	3.2	10.3	2.5	21,040	1,660	19,380	4,050	16.2	9.2	25.4	—	+	+	+
13	Above Hamilton Avenue (near sewer outlet)	..	85	0.7	0.4	1.1	8.5	17,720	540	17,180	5,100	6.9	3.0	9.9	—	+	+	+
14	Below Hamilton Avenue (opposite sewer outlet)	51°.8 F.	80	6.0	4.8	10.8	2.0	24,320	12,360	11,960	5,200	13.3	5.0	18.3	296,000	+	+	+
15	Entrance to bay	50°.0 F.	70	..	..	9.3	3.5	19,900	6,360	13,540	6,950	7.1	7.7	14.8	335,000	+	+	+

NOTE. — Samples taken on a rising tide.

[1] Milky.

due to the large amount of clean water discharged from the power house. At Third Street the curve rises to what would be a point on the normal dilution curve. Opposite the Fifth Street basin there is a rapid rise, which is due to a stirring up of the water at that point by tugs at the time that the sample was taken. The curve then again drops rapidly,

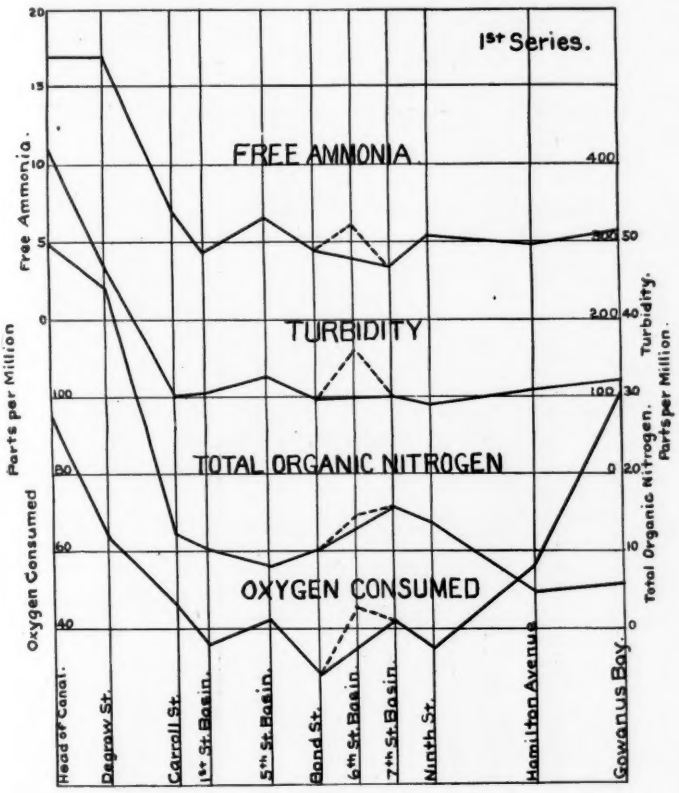

FIG. 10

but not to what would be a point on the normal dilution curve. The Bond Street sewer enters here. There is then a gradual drop until we arrive at the Tartar Chemical Company, where there is a sudden increase. Above Hamilton Avenue bridge there is another quick drop. A glance at some of the other curves shows that this drop is general. On the other side of the bridge, however, the curve rises again.

A sewer enters here. There is then a slow, gradual decrease, indicating dilution with sea water.

The curves for suspended and dissolved organic nitrogen are similar to that for the total organic nitrogen, and no special comment on them is necessary.

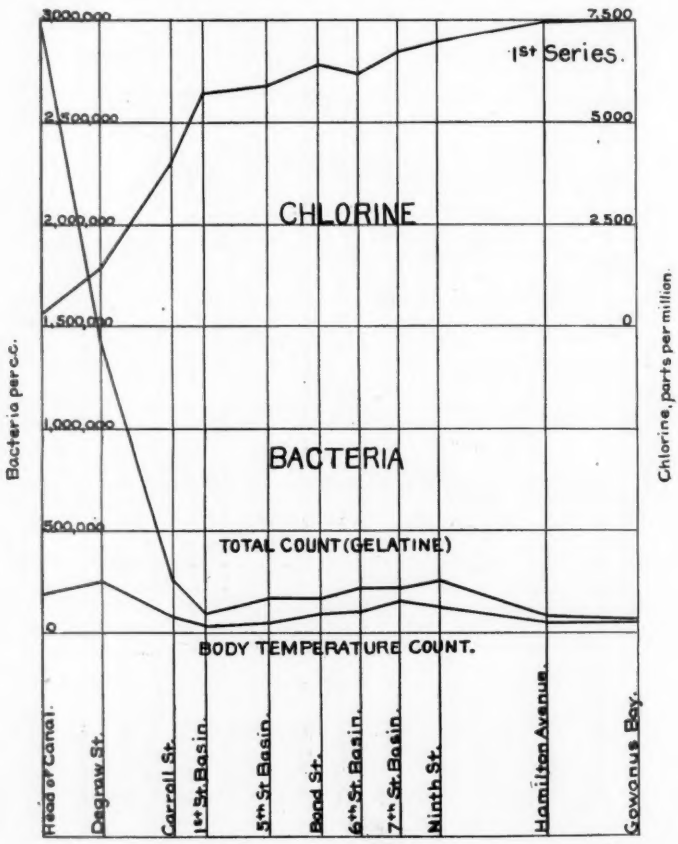

FIG. 11

Oxygen Consumed. — In the first series (Fig. 10) this curve falls off rapidly until after Bond Street is passed. Opposite the Fifth Street basin there is an increase, probably due to coal dust. The most conspicuous part of the curve, however, is the steady and rapid increase after the starch factory at Ninth Street is passed.

In the second series (Fig. 13) there is an increase at the start, with a quick rise at Carroll Street. A glance at the turbidity curve will show that this rise is due to the water having been stirred up. There is a quick drop at the First Street basin and a quick rise again at Third Street. The turbidity also is high at this point. The appar-

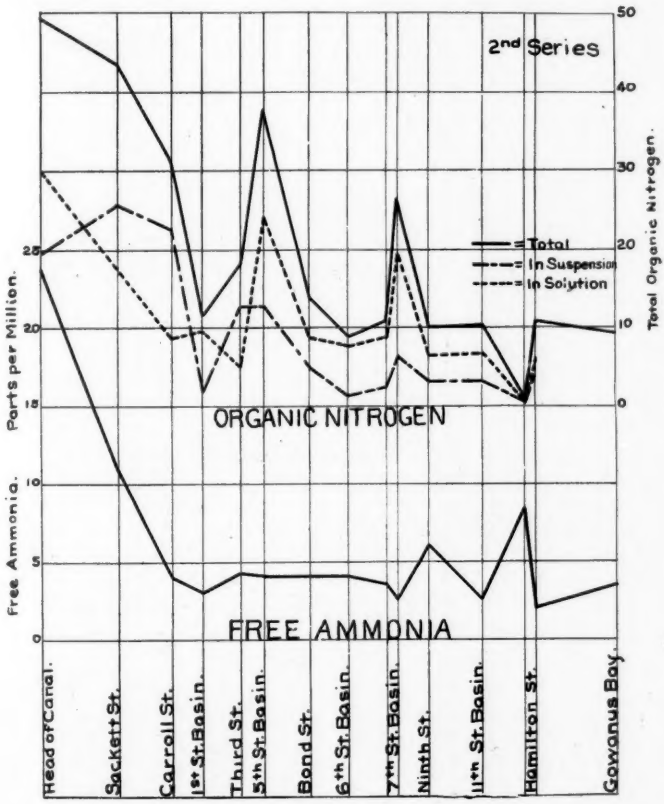

FIG. 12

ent drop at the Fifth Street basin was unexpected, since the nitrogen is high at that point. A further study of the diagrams, however, will show that the oxygen consumed is also absolutely very high.

After passing Bond Street the curve has a downward tendency, with only a slight rise beyond Ninth Street. This is significant. The samples were taken on a Monday morning, and there was no pollution

then by the starch factory. Most of the material which had been discharged on Saturday night was flushed out by the heavy flow of storm water on Saturday night and Sunday.

The same drop just above the Hamilton Avenue bridge already

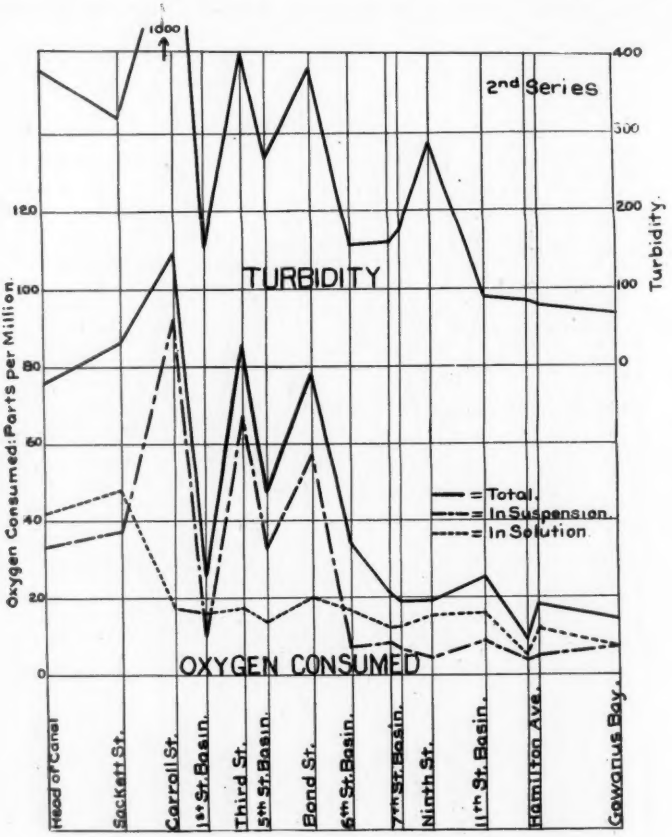

FIG. 13

mentioned in the discussion of the organic nitrogen curve is conspicuous here. Below Hamilton Avenue the curve rises again and then decreases gradually.

Turbidity. — In both series of analyses (Figs. 10 and 13) this curve seems to vary with the dilution and shows that sedimentation has taken

place all the way down, being interrupted occasionally by the stirring up of the water. The curves for turbidity are strikingly similar to those for organic nitrogen and for oxygen consumed.

The remaining curves simply reënforce points brought out in the

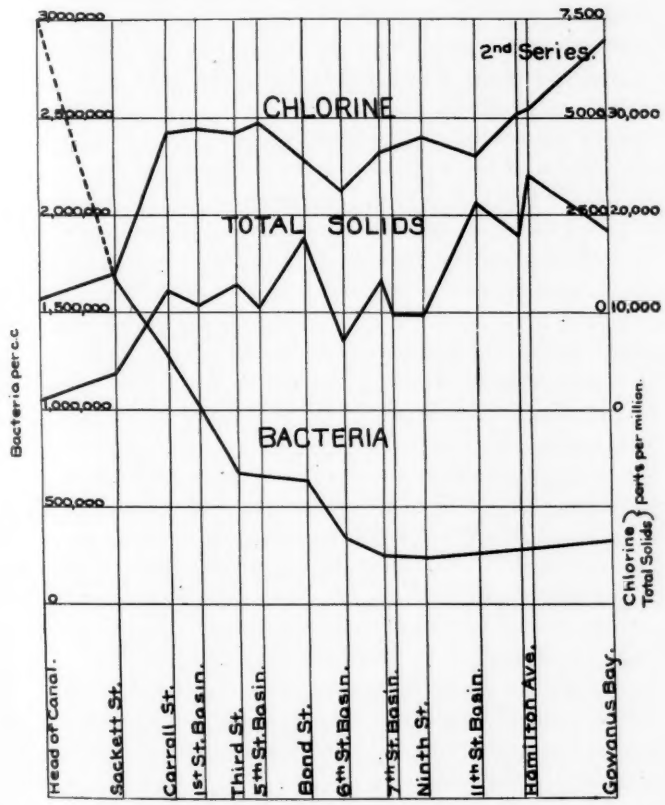

FIG. 14

curves already discussed and require no especial explanation. We are, therefore, ready to consider the various curves simultaneously. Sample No. 1 shows at once that we have much accumulated solid matter which is constantly stirred up. The nitrogen is very high. This means that there is an additional supply of organic matter there, which, being constantly stirred up, keeps in circulation, but is never carried out. This

effect is not lost all the way down the canal. The fact that the chlorine is above the normal — twice what it ought to be — shows a mixture of sea water with the sewage. In the first five samples the ratio of dissolved nitrogen to total nitrogen gives good evidence of septic action. Since organic nitrogen is converted into free ammonia, there are two changes noticeable: the ratio of free ammonia to total organic nitrogen and the ratio of oxygen consumed to total organic nitrogen becomes greater. Both carbon and nitrogen are going down, but the nitrogen goes down much faster.

From a bacteriological standpoint, the low count at body temperature as compared with the high total count in water from the head of the canal is interesting. It indicates that septic action is taking place and corroborates the evidence mentioned in the last paragraph.

The total number of bacteria falls off very rapidly on going down the canal, reaching in the first series of analyses (Fig. 11) a minimum opposite the First Street basin. In the second series (Fig. 14) this minimum is not reached until the Seventh Street basin is reached, showing the flushing effect of the storm water. A glance at the curves for chlorine shows that this rapid decrease in the total bacteria count is due to dilution.

Below the First Street basin the number of bacteria does not increase materially, thus substantiating the evidence that most of the pollution below this point is due to industrial wastes.

The discharge of the Bond Street sewer seems to increase the oxygen consumed, but not the nitrogen. The bacteria go down, and this sewage seems to be an antiseptic, non-nitrogenous substance, in appearance quite similar to gas plant wastes.

Lateral Basins. — In the first series, to ascertain how the water in the basins compared with that in the main part of the canal, a sample was taken from one of these. This is represented in the curve (Fig. 10) by dotted lines. The result is significant. A glance at the curves shows that free ammonia, oxygen consumed, total organic nitrogen, turbidity, and the total bacteria count are higher than in the adjacent portion of the main canal, while the chlorine and the body temperature count are lower. This is characteristic of a dead end. The depression in the chlorine curve shows that the tide exerts no flushing effect, and the low body temperature count shows that the water in the basin is stagnant.

Variations between the Two Series. — The first series of analyses was carried on at a time when there was no rain. The second series

of samples was taken after the run off from a heavy rainfall had stirred up the contents of the canal. On comparing the two sets of curves, the reader will see that in general they cross one another several times, that the curves of the second series are very ragged, plainly giving evidence of a general stirring up. At the uppermost point of the canal, however, the second series shows less pollution than the first. The curves soon cross, however, and in general the first series of curves is lower than the second. This is due to the large volume of storm water which had pushed the sewage at the head end farther down. The turbidity curve for the second series is entirely above that for the first series.

Difference in Character of Pollution in Various Parts of the Canal.— The upper part of the canal is badly polluted by sewage. At the lower end the pollution is largely industrial wastes mixed with more or less sewage.

As a rule, the amount of nitrogen present varies directly with the amount of sewage. The other constituents of sewage vary with the nitrogen. Therefore when the nitrogen is greatly increased without a corresponding increase in the other sewage substances it is an indication of industrial wastes. This is exactly what happens in that portion of the canal opposite the Tartar Chemical Company. On talking with one of their employees, we learned that crude argol is digested with sulphuric acid, and that the waste product is an acid sludge running high in sulphates and nitrogen.

In the first series, below Ninth Street the oxygen consumed curve went up rapidly. In the second series the curve had a downward tendency. The starch factory, not running on Sunday, had no waste to discharge at that time. The abnormal values for the oxygen consumed are probably due to gluten in the wastes discharged by the starch factory.

Another interesting point, characteristic of both series of curves, is the sudden drop in most of the curves just above Hamilton Avenue. It is significant that not only the organic nitrogen, oxygen consumed, turbidity, and total solids, but the bacteria also go down. This looks like precipitation. The curves for ammonia and chlorine, on the other hand, show a slight increase. Immediately above this point is a coal gas plant, which evidently uses lime to recover its ammonia. The waste from the Tartar Chemical Company, which is carried along by the tide, comes into contact with the gas plant waste, and calcium sulphate is

probably precipitated, carrying down with it nearly all the other suspended matter.

The rapid decrease in bacteria below Bond Street gives evidence of antiseptic action. A glance at the diagrams will show that, although the nitrogen and carbon go up at that point, the ammonia remains the same, and the bacteria count goes down and stays down. The fact that the ratio of carbon to nitrogen is greatly increased shows that the pollution from the Bond Street sewer is largely of a carbonaceous nature.

Although taken at different times, and thus representing different conditions, there is no essential difference in the results obtained from the two series. The second series simply reënforces the first and justifies drawing the following conclusions:

The canal is highly polluted with house drainage and industrial wastes. The city sewers are the chief source of the trouble. The organic animal matters contained in the sewage are more easily susceptible to putrefactive influences than is the vegetable matter in the industrial wastes. The tide exerts very little flushing effect in the main body of the canal, and practically none whatever in the dead ends or basins.

Summary of Existing Conditions

The table below will show the immense pollution of the canal. The figures for sea water were taken from the Report of the Committee on the Charles River Dam. The figures for Boston tap were taken from the Massachusetts Board of Health Report for 1904. Those for harbor water are the average of the accompanying table, compiled from analyses made by Dr. Jackson for the New York Bay Pollution Commission.

Sample.	Free NH_3.	Organic nitrogen.	Oxygen consumed.
From head of canal	24.0	50.1	85.4
Sea water	0.012	0.16	. .
Boston tap	0.015	0.29	3.9
Harbor water	0.534	1.28	. .

The figures speak for themselves. The pollution of the canal is almost fifty times that of the harbor.

TABLE III.—SHOWING ANALYSIS OF SAMPLES FROM THE EAST RIVER, MADE BY DR. DANIEL D. JACKSON FOR THE NEW YORK BAY POLLUTION COMMISSION

CHEMICAL ANALYSIS (Parts per Million)

No.	Date of collection.	Place of collection.	Temperature.	Turbidity (parts per million of silica).	Tide.	Nitrogen as			Chlorine.	Dissolved oxygen; c.c. per liter.	Number of bacteria per c.c., 48 hours at 20° C.	B. Coli		
						Albuminoid ammonia.	Free ammonia.	Nitrites.				In 0.1 c.c.	In 1 c.c.	In 10 c.c.
	April 1, 1905, A.M.													
1	9.55	Off Battery (bottom)	—	7	Flood	0.27	0.31	. .	11,800	8.62	4,280	+	+	+
2	10.00	Off Battery (surface)	—	10	Flood	0.27	0.32	. .	6,100	8.84	6,250	+	+	+
3	10.05	East River off Pier No. 15	. .	10	Flood	—	—	. .	4,800	. .	4,410	+	+	+
4	10.10	Under Manhattan Bridge	—	8	Flood	0.32	0.49	. .	9,600	. .	8,460	+	+	+
	Jan. 30, P.M.													
9	12.35	Off Battery and Governor's Island (midstream, 5 feet from surface)	37°.0 F.	45	Flood	0.78	0.97	0.012	7,600	8.50	1,510	+	+	+
8	12.30	Off Battery and Governor's Island (midstream, 40 feet from surface)	37°.0 F.	30	Flood	0.73	0.84	0.015	11,600	—	920	+	+	+
7	12.20	Off Battery and Governor's Island (midstream, 80 feet from surface)	37°.0 F.	35	Flood	0.73	0.75	0.012	12,700	—	760	+	+	+
12	3.15	Off Battery and Governor's Island (midstream, 5 feet from surface)	. .	18	Ebb	0.73	1.11	0.013	9,100	8.60	1,200	+	+	+
11	3.10	Off Battery and Governor's Island (midstream, 40 feet from surface)	. .	20	Ebb	0.67	0.70	0.012	13,100	—	740	+	+	+
10	3.00	Off Battery and Governor's Island (midstream, 80 feet from surface)	. .	25	Ebb	0.71	0.72	0.011	13,200	—	540	+	+	+
		Series No. 6												
27	3.38	Off Battery	33°.0 F.	6	. .	0.28	0.36	. .	8,300	. .	7,280	+	+	+
28	3.45	Off Pier No. 6, East River	33°.5 F.	—	. .	—	—	. .	8,400	. .	14,100	+	+	+
29	3.55	Off Pier No. 13, East River	33°.5 F.	10	. .	0.24	0.41	. .	8,600	. .	18,400	+	+	+
30	3.58	Off Pier No. 20, East River	33°.5 F.	5	. .	0.21	0.37	. .	8,900	. .	12,600	+	+	+
31	4.00	Off Pier No. 28, East River	33°.5 F.	7	. .	0.40	0.52	. .	8,400	6.98	15,300	+	+	+
32	4.05	Off Pier No. 23, East River (Brooklyn)	33°.5 F.	—	. .	—	—	. .	8,600	. .	4,300	0	0	+
33	4.15	Off Atlantic Docks, Buttermilk Channel	33°.5 F.	8	. .	0.25	0.40	. .	8,600	6.54	10,400	+	+	+
35	4.25	Gowanus Bay	. .	7	. .	0.35	0.74	. .	8,600	5.63	8,500	+	+	+
36	4.35	Gowanus Canal, Hamilton Avenue Bridge	. .	10	. .	1.11	7.00	. .	6,800	. .	270,000	+	+	+

Absolute Values Compared with Sewage. — Below is given a table comparing the canal water with several well-known sewages.

Place.	Date.	Free NH_3.	Organic Nitrogen.		Chlorine.	Oxygen consumed.	Bacteria per c.c.
			Total.	Solution.			
Brooklyn	April 14, 1906	36.0	71.3	51.8	230.0	165.0	3,120,000
Boston	Average	19.9	23.0	10.5	1,300.0	45.0	3,000,000
Lawrence	Maximum, 1904	71.8	39.2	20.6	163.9	65.4	3,020,000
Lawrence	Minimum, 1904	41.6	12.1	5.4	82.7	38.4	1,440,000
Lawrence	Average, 1904	51.5	18.3	8.7	123.1	48.6	1,930,000
Andover	June, 1902	103.0	51.4	20.0	678.0	107.7	3,680,000
Andover	Average, 1902	74.6	35.8	17.0	164.7	76.7	3,750,000
Head of canal	Mean	24.0	50.1	30.5	325.0	85.4	3,100,000
Opposite Fifth Street basin	Mean	7.5	37.6	24.8	4,850.0	46.5	670,000
Below Hamilton Avenue	Mean	3.5	7.8	4.5	6,325.0	18.3	200,000

From the above table it is evident that the water at the head of the canal is about two-thirds as strong as Brooklyn sewage. It is more than twice as strong as Boston sewage; its strength is three times that of Lawrence sewage and about equal to that of Andover, which is one of the strongest in Massachusetts.

The sample taken opposite the Fifth Street basin corresponds to the strongest Lawrence sewage in 1904, and to the average Andover sewage for 1902.

At Hamilton Avenue the water contains about one-tenth of Brooklyn sewage, and is about one-half the strength of the minimum Lawrence sewage in 1904.

Recommendations, with Calculation of the Amount of Water to be Pumped

Recommendations. — The Gowanus Canal is in a very poor sanitary condition, and measures should be taken to abate this nuisance as soon as possible. In the study from which this abstract is taken, the methods of dealing with this problem came under two heads, those which involve some method of flushing the canal and those involving a sewerage system for the locality. These were taken up and considered in detail by

the writer's colleague in the investigation — Mr. Norman P. Gerhard, now assistant engineer, Board of Water Supply, City of New York.

It is not the purpose of this abstract to suggest a remedy, since the problem has already received the attention of the engineers of the Borough of Brooklyn and a flushing tunnel from the East River to the head of the Gowanus Canal is now under construction. The writer will therefore confine himself, as he did in the original thesis, to a calculation of the amount of water to be pumped under various methods of flushing the canal.

Calculations were made in two cases. In the first it was assumed that flushing alone would be considered and enough water pumped in to render the sewage matter innocuous and to create a current strong enough to prevent it from settling out. In the second case it was assumed that intercepting sewers would be built and the district sewered, enough water being pumped to cleanse the canal in a reasonable length of time, and thereafter create a small current sufficient to prevent it from becoming stagnant.

Both methods require that the present sludge deposits should be removed by dredging. A tremendous quantity of water would be required to give sufficient scouring velocity to remove the sludge. Even so, the present nuisance at the head of the Gowanus Canal would only be transferred to its branch dead ends and into Gowanus Bay. The power of New York Harbor to dispose of the sewage that comes into it is already being questioned. The Harbor Pollution Commission found that the tide has little effect in eliminating the pollution of the bay, and that the water seems incapable of renewing its supply of oxygen. It is evident then that it would be unwise to pollute the harbor still more by flushing into it the sludge which has accumulated in the Gowanus Canal.

Calculation of the Amount of Water to be Pumped. — We have, therefore, to consider for calculation two possibilities, the daily dilution of the total amount of sewage discharged into the Gowanus Canal, and the remedying of its present unsanitary condition in case an intercepting sewer should be built. The object of these calculations is to compute the required dilution from figures obtained by chemical analyses. Before proceeding with these calculations it is necessary, however, to determine first the proportion of sewage at present in the canal.

Sewage Density. — This may be defined as the proportion of sewage per unit volume. The canal water can be considered as a mixture of

three separate liquids: sewage, terrestrial (*i.e.*, surface + ground) water, and harbor water. The object of these calculations is to obtain absolute values for each of these three. In making these calculations, use has been made of the usual method of determining by the chlorine content in a mixture of two such liquids the proportion of each. This gave two independent equations. A third equation was obtained by means of the nitrogen values. The method of attack was as follows:

Consider a section in the canal of unit dimensions. Let

x = portion of sewage;
y = portion of terrestrial water;
z = portion of harbor water;
C = total chlorine;
N = total nitrogen;
c_1 = chlorine in sewage;
c_2 = chlorine in terrestrial water;
c_3 = chlorine in harbor water;
n_1 = nitrogen in sewage;
n_2 = nitrogen in terrestrial water;
n_3 = nitrogen in harbor water.

We then have the equations:

$$x + y + z = 1. \tag{1}$$

$$xc_1 + yc_2 + zc_3 = C. \tag{2}$$

$$xn_1 + yn_2 + zn_3 = N. \tag{3}$$

To solve we must find or assume values for the constants. The pollution of the canal is so great that the amount of nitrogen in terrestrial water when compared with it is practically zero. Considering the proximity to the sea, we may assume 10 as an average value of the chlorine content of this water.

From the table given above, showing the analyses made by Dr. Jackson for the New York Bay Pollution Commission, it appears that average figures for the nitrogen and chlorine content of harbor water may be assumed at 1 and 8,600, respectively.

Considering the particular problem on hand, we therefore have the following constants:

$$c_1 = 230;\ c_2 = 10;\ c_3 = 8{,}600;$$

$$n_1 = 107;\ n_2 = 0;\ n_3 = 1.$$

Substituting these values in the above equations, the two following tables, showing the proportion of sewage, terrestrial water, and harbor water at different sections in the canal, have been computed:

FIRST SERIES

No. of sample.	C.	N.	Proportion of		
			Sewage.	Terrestrial water.	Harbor water.
1	300	67.4	.63	.36	.01
2	1,400	61.0	.57	.42	.01
3	4,000	19.2	.18	.35	.47
4	5,700	14.8	.13	.19	.68
5	5,900	14.8	.13	.14	.73
6	6,400	14.8	.13	.08	.79
7	6,200	20.9	.19	.03	.78
8	6,700	19.2	.17	.03	.80
9	7,000	19.2	.17	.03	.80
10	7,450	9.6	.08	.09	.83
11	7,500	19.2	.17	.03	.80

SECOND SERIES

No. of sample.	C.	N.	Proportion of		
			Sewage.	Terrestrial water.	Harbor water.
1	350	73.8	.69	.31	.01
2	1,010	54.5	.51	.35	.14
3	4,600	35.3	.32	.05	.63
4	4,700	14.4	.13	.33	.54
5	4,600	22.4	.13	.29	.58
6	4,850	41.6	.38	.05	.57
7	3,890	17.6	.16	.36	.48
8	3,100	12.8	.12	.51	.37
9	4,100	14.4	.13	.38	.49
10	4,200	28.8	.26	.24	.50
11	4,480	16.0	.15	.33	.52
12	4,050	12.8	.12	.42	.46
13	5,100	9.6	.08	.34	.58
14	5,200	12.8	.12	.28	.60
15	6,950	12.8	.11	.10	.79

Calculation of Quantity of Water to be Pumped. — One condition of the degree of dilution required to make sewage inoffensive is that the diluting water shall have a sufficient supply of free oxygen. The experiments made on Brooklyn sewage for putrescibility showed the dilution of 1 : 15 to be necessary.

The sewage discharged into the canal daily is estimated to be 793,000 cubic feet. The amount of water, therefore, to make this innocuous is 793,000 × 15 = 11,895,000 cubic feet per day. Allowing a factor of safety of 2, there would be required 23,800,000 cubic feet per day.

Supposing no sewage is allowed to enter the canal and its contents are to be flushed out in thirty days, we can calculate the necessary quantity of water as follows:

The average sewage density of the canal, as computed in the above tables, is 0.25. Therefore $x = \frac{10{,}000{,}000\ (0.25)\ (15)}{30} = 1{,}250{,}000$ cubic feet per day.

The amount of water to be pumped was also calculated by a method based on the amount of oxygen available from East River water and the average amount of oxygen consumed by water in the canal. Although there is no evidence that sewage requires oxygen equivalent to its oxygen consumed value to oxidize it under natural conditions, this calculation is interesting in that the two methods of calculation used gave practically the same result. For this reason the writer thought this calculation from chemical data might be of general interest, and has included it in this report.

This calculation was based on the assumption that the volume of the canal water and the amount of oxygen consumed by it bears some relation to the amount of water to be pumped and the free or dissolved oxygen in it. We can express this relation algebraically as

$$xO_d = KSO_c$$

where x = quantity of East River water to be pumped in cubic feet per day.

O_d = amount of dissolved oxygen in parts per million in the water to be pumped.

S = amount of sewage to be oxidized in cubic feet per day.

O_c = oxygen consumed by S in parts per million.

K = ratio of amount of dissolved oxygen in flushing water to amount required to oxidize the organic matter.

If O_d is all to be used up, K becomes unity, and the quantity to be pumped is $x = \frac{SO}{O_d}$.

It appears from analyses made of East River that 7.5 c.c. per liter is a fair average value for O_d.

Weight of liter O = 1.429 grams.
Weight of 1.0 c.c. O = 0.00143 gram.
Weight of 7.5 c.c. O = 0.0107 gram.

Therefore $O_d = 10.7$ parts per million and $x = \frac{SO}{10.7}$.

We will compute first the amount of water needed to render innocuous the sewage discharged into the canal. The total sewage discharged into the canal was estimated at 793,000 cubic feet per day. $O_c = 165$ parts per million. Therefore $x = \frac{793{,}000 \times 165}{10.7} = 12{,}200{,}000$ cubic feet per day.

If we allow a factor of safety of 2 to cover future increase of sewage flow, x would equal $12{,}200{,}000 \times 2 = 24{,}400{,}000$ cubic feet per day.

The amount of water needed for flushing the canal, supposing no more sewage is allowed to enter and thirty days are allowed for flushing, was computed as follows. The volume of the canal water is 10,000,000 cubic feet. S in our formula would then be $\frac{10{,}000{,}000}{30} = 333{,}330$ cubic feet per day. The average value for O_c is 46.1. Then

$$x = \frac{333{,}330 \times 46.1}{10.7} = 1{,}440{,}000 \text{ cubic feet per day.}$$

Summing up these calculations, it appears that if sewage is allowed to continue discharging into the canal perhaps 25,000,000 cubic feet of water will have to be pumped daily to dilute the canal water sufficiently to render it innocuous. If the district is to be sewered, 1,500,000 cubic feet per day will be necessary.

Summary and Conclusions

The Gowanus Canal in its present condition is unsanitary and a nuisance. Sewage enters the canal and stays there. The heavier particles settle out at once, forming banks in front of the outlets of the sewers. The light, flocculent matter moves up and down with the tide and is gradually deposited, silting up all portions of the canal.

The water being devoid of oxygen, this sludge then undergoes putrefaction. Inasmuch as the temperature of 65° to 70° F. is sufficient to cause the sludge to give off putrid gases and the average temperature of the canal even in the winter time is about 70° F., it is easily seen why the nuisance exists all the year round.

In proceeding to summarize the results from the special point of view of this investigation, an attempt will be made to answer the questions raised in the first portion of this part of this report.

The odors of the factories are distinct from those of the canal and are not offensive. The bad smells are due to the putrefaction of nitrogenous matter in the sewage and sludge.

The water which now fills the canal is a mixture of sewage, terrestrial, and harbor water. At the head of the canal the water is 0.65 sewage, 0.34 terrestrial water, and 0.01 harbor water. At Hamilton Avenue it is 0.10 sewage, 0.20 terrestrial water, and 0.70 harbor water. The average sewage density of the whole canal is 0.25. Brooklyn sewage is much stronger than Massachusetts sewages. The water at the head of the canal is slightly stronger than Andover sewage, and the average value of the whole canal corresponds very nicely to Lawrence sewage.

The amount of organic matter present is very large, and to destroy it would require an amount of oxygen equivalent to that contained in $\frac{10{,}000{,}000 \times 0.25 \times 165}{10}$ = say to 45,000,000 cubic feet of harbor water, which is about 75 per cent. saturated. The amount of putrescible substances present is large, and their oxidation is probably inhibited by antiseptic wastes contributed by the Bond Street sewer. The storm sewers bring down much matter which is indifferent to chemical change and which, silting up the canal, makes constant dredging necessary. The average of analyses on the sludge shows the amount of this to be about twice that of the organic matter present.

The pollution due to the factories is largely vegetable carbonaceous and nitrogenous organic matter. The Tartar Chemical Company and the starch factory contribute most of this. The amount of this waste, however, is small when compared to that contributed by the city sewers.

The canal water is about fifty times as much polluted as that in the part of the harbor adjoining its outlet; the ebb and flow of the tide do comparatively little toward renewing the water in the canal, the water in the latter practically simply surging back and forth.

The water required for pumping after dredging has taken place depends upon the method used. The amount required to render innocuous the sewage which is discharged into the canal and to provide for future increase is perhaps 25,000,000 cubic feet per day. To flush out the present contents in thirty days 1,500,000 cubic feet of East River water would be required daily. Therefore if flushing alone were resorted to 25,000,000 cubic feet per day are necessary. If the district is first sewered and the canal then flushed 1,500,000 cubic feet would be required daily.

THE DETECTION OF CARAMEL IN VANILLA EXTRACT

By A. G. WOODMAN and E. H. NEWHALL

THE detection of caramel when present in the small quantities used for coloring beverages, vinegar, or extracts is not a simple matter. Comparatively few methods have been proposed for this, and most of the tests are of a negative rather than positive character. Some of these negative methods have been shown to be of considerable value in such special cases as in distinguishing caramel from the natural color of whisky, but are not suited, necessarily, for such material as extract of vanilla. The only method given among the Official Methods of Analysis [1] is that depending on the color remaining after treatment with basic lead acetate, a method which, as will be shown later, is open to considerable objection. A thorough review of the literature indicated that the following methods were of value to study for use with extracts of vanilla: Of positive methods, precipitation with paraldehyde (the Amthor test) and precipitation with phenyl-hydrazine; of negative methods, depending in general upon the selective action of solvents or other reagents on the natural color, the fuller's earth test, and the test with basic lead acetate.

Preliminary Experiments.—Before studying the above mentioned methods in detail it was found advisable to review the action of the common organic solvents on caramel solutions, with the possibility of finding a solvent immiscible with water which would remove the caramel color directly from the extract. To this end, aqueous solutions of caramel were shaken in separate tests with ether, chloroform, petroleum ether, acetone, benzene, ethyl acetate, amyl acetate, ethyl benzoate, and carbon tetrachloride. In no case was any color found in the layer of added solvent. Of the solvents miscible with water only methyl alcohol and allyl alcohol had any appreciable solvent action. The use of methyl alcohol has already been proposed by Fradiss,[2] but it is necessary to

[1] U. S. Dept. Agr., Bur. of Chem., Bull. 107, p. 159.

[2] Ztschr. Zucker Ind., **28**, 229.

employ it upon the dried residue. The solubility of caramel in methyl alcohol was found by experiment to be 8.232 grams per liter at 20°.

Paraldehyde Test.—This test, originally proposed by Amthor,[1] has found considerable application, especially in the examination of distilled liquors. In its original form it may be briefly summarized as follows: 10 c.c. of the liquid, contained in a tall, narrow glass, are mixed with 30–50 c.c. of paraldehyde, and absolute alcohol is added until the liquids are homogeneous. If caramel is present, at the end of twenty-four hours a brownish yellow or dark brown precipitate is formed.

A number of tests were made on solutions of caramel in studying the modifications of this procedure. It has been questioned whether the precipitate formed is caramel or a compound of caramel with paraldehyde. Experiment indicated, however, that the substance is in all probability caramel. It was brown and flocculent, resembling caramel in appearance. It was not sufficiently soluble to impart any color to warm methyl or ethyl alcohol when poured through the filter. In warm water, however, it was readily soluble, giving a dark brown solution. This solution had approximately the same reducing power on Fehling's solution as did a caramel solution of the same color. It is quite probable that the phenomenon observed in the paraldehyde test is only one of lessened solubility.

The relative volumes of paraldehyde and colored solution are matters in regard to which there appears to be considerable difference of opinion among those who have made use of the test. Experiments indicated that the paraldehyde should be largely in excess. For example, volumes of paraldehyde less than those of the caramel solution failed to give a precipitate within forty-eight hours. With equal volumes of paraldehyde and of caramel solution less than half the tests gave a precipitate within a day. The order in which the reagents were added had no effect on the results. In all of these experiments only sufficient alcohol to make the solutions homogeneous was added, as an excess of alcohol was found to be detrimental.

In regard to the effect of temperature on the precipitation it was found as a result of numerous trials that no advantage was gained by employing a temperature other than that of the laboratory.

The delicacy of the test is not very great. Tests made in triplicate showed that a precipitate can be obtained with a caramel solution of a

[1] Ztschr. anal. Chem., **24**, 30.

concentration of 1 gram of caramel in 1,343 c.c. of water, whereas tests made with half that concentration failed. This would correspond to 0.00372 gram of caramel in the 5 c.c. used for the test.

To summarize, repeated trials showed the best procedure for the test to be as follows: To 5 c.c. of the aqueous solution add 15 c.c. of paraldehyde, then carefully add, with frequent shaking, just enough alcohol to make the solutions mix. Let the solutions stand over night. No advantage was found in the use of the centrifuge for collecting the precipitate. The proportion of reagents given here is the same as advocated by Amthor in the original description of the test. Amyl alcohol can be used instead of paraldehyde, as would be expected if the phenomenon were only one of lessened solubility, but offers no special advantages over the other reagent.

When the paraldehyde test was applied to vanilla extracts of known purity some difficulty was experienced. With some extracts, notably with those prepared strictly according to the United States Pharmacopœia, a gummy, brown substance was deposited on standing over night; in fact, in some cases within half an hour. This was found to be a mixture of resins and sugar, thrown out by the addition of alcohol and paraldehyde. While this precipitate did not greatly resemble caramel, it would effectually obscure it if present in slight amount.

The separation of the resins and sugar from the extract prior to making the test was a matter that caused some trouble. The resin was removed without much difficulty by evaporating the original extract to one-third its volume, making up with hot water and filtering. After numerous experiments it was found best to separate the caramel and sugar by a preliminary treatment with zinc hydroxide, as described under the phenyl-hydrazine test.

Phenyl-Hydrazine Test.—The results obtained by this test were, on the whole, better than those given by the preceding test. The solution used was a solution of two parts phenyl-hydrazine hydrochloride and three parts sodium acetate in twenty parts water. In making the test equal volumes (5 c.c.) of the reagent and the caramel solution were mixed and allowed to stand over night, the formation of a brown precipitate being noted. This test was found somewhat more delicate than the paraldehyde test, giving good results when the concentration of the caramel was reduced to 1 gram in 7,633 c.c. of water. When no caramel was present, a ring of brown flakes sometimes formed at the surface of the liquid, but these would not readily be mistaken for the caramel precipitate, which is flocculent.

It was found best in the case of extracts to concentrate the caramel by a preliminary treatment with zinc hydroxide, consisting in adding zinc chloride and potassium hydroxide to the extract, filtering the precipitate, and dissolving it in acetic acid. This solution, after being neutralized and concentrated, was found to be well adapted to either the paraldehyde or phenyl-hydrazine test. In some cases pure extracts were found to give a light gray precipitate containing zinc, but which did not resemble caramel. Fuller's earth can be used instead of the zinc hydroxide,[1] but considerable time is required to wash the earth with cold water, and on boiling with water to extract the caramel the volume of liquid is much greater than with zinc hydroxide. The zinc treatment is simpler and gives equally good results.

Use of Absorptive Reagents.—The reagent of this kind most widely used is fuller's earth, a test based on its property of removing caramel from aqueous solutions having been found to give good results in the case of spirits.[2] The test consists in adding 25 grams of fuller's earth to 50 c.c. of the suspected sample, filtering after half an hour and determining the percentage loss in color.

Quantitative tests were made of the applicability of this and other absorptive agents to vanilla extracts. The color measurements were made by means of a Duboscq colorimeter. Fuller's earth was found to remove 99 per cent. of the color when 30 c.c. of an aqueous solution of caramel of about the color of a vanilla extract were shaken with 15 grams of the earth. The percentage loss of color with a pure extract, however, under similar conditions was found to be 88 per cent. It is evident that the difference noted is much too slight to permit any point to be fixed as to just how much color an extract may give up in this manner and still be accounted a genuine product. The same objection to the fuller's earth test has been found by others in the case of vinegar.[3] Nevertheless, this method has been copied extensively and will be found given in standard works as the best method for detecting caramel in vanilla.

Basic lead acetate, as previously stated, has been recommended to remove the natural color of vanilla extract, the assumption being made that any brown or yellow color remaining is due to caramel. Quanti-

[1] U. S. Dept. Agr., Bur. of Chem., Bull. 65, p. 71.

[2] Crampton and Simons, Jour. Am. Chem. Soc., 21, 355.

[3] W. L. Dubois, U. S. Dept. Agr., Bur. of Chem., Bull. 105, p. 23.

tative measurements showed that 95 per cent. of the natural color was removed and likewise 43 per cent. of the caramel color. It is evident that with no further criterion than the color of the filtrate the analyst would find it hard to state whether a pale yellow filtrate was due to caramel, 43 per cent. of which was retained on the filter, or whether it was the residual color from a pure, highly colored extract.

In the case of kaolin, the removal of color from caramel solutions was found to be 86 per cent.; from vanilla extracts, 76 per cent. Zinc hydroxide removed 92 per cent. from a caramel solution, and 78 per cent. from a pure extract, the difference in each case being too slight to permit the development of a satisfactory test. In brief, all of the absorptive reagents tried had appreciably similar action on caramel and vanilla, and hence have little practical value except to concentrate the caramel for some further test.

Color Quotient.—It will be remembered that no immiscible solvent was found which had any action on a caramel solution when shaken with it. It was therefore determined to endeavor to remove the natural vanilla color and leave the caramel. A number of solvents were tried successfully, ethyl acetate, amyl alcohol, and ether giving the best results. Of these, the best was probably the ethyl acetate, which removed 60 per cent. of the vanilla color and practically none of the caramel. If, now, an adulterated extract were treated with ethyl acetate, much of the natural color would be removed and but little of the caramel. A subsequent treatment with fuller's earth would give a much greater percentage loss of color than if applied to the original extract. The consideration of these facts led to the formulation of a new test for caramel, the procedure of which may be stated as follows:

A 35 c.c. sample, procured by diluting the original extract if necessary, is evaporated on the water bath to one-third its volume, to remove the alcohol and the loss made up by the addition of water. The dealcoholized extract is shaken in a separatory funnel with three successive portions of 15 c.c. each of ethyl acetate. After the last portion has been separated, part of the aqueous layer is saved for comparison and 30 c.c., or as much as possible, of the remainder is shaken with 15 grams of fuller's earth, allowed to stand for half an hour, and filtered. The percentage of color removed by ethyl acetate divided by the percentage of color removed by fuller's earth gives the "color quotient." A standard extract made according to the Pharmacopœia gave a color quotient of 2.30, whereas a caramel solution gave 0.276.

Comparison of Tests on Commercial Samples.—The method just described was compared with the other three methods on a number of pure and of adulterated vanilla extracts. For convenience the other methods are repeated here:

Paraldehyde and phenyl-hydrazine tests: 15 c.c. of the extract are mixed with 2 c.c. of zinc chloride (5 per cent. solution), and 2 c.c. of caustic potash (2 per cent. solution) are added. The precipitate is filtered, washed with hot water, and dissolved in 15 c.c. acetic acid (10 per cent. solution). This is concentrated to about half its volume, the excess of acid neutralized, and the solution divided between two test tubes. To one of these three volumes of paraldehyde are added, and just sufficient alcohol to make the mixture homogeneous. To the other tube an equal volume of a mixture of two parts phenyl-hydrazine hydrochloride, three parts sodium acetate, and twenty parts water is added. Both tubes will show a brown, flocculent precipitate after standing over night if caramel be present.

Basic lead acetate test: 10 c.c. of the extract are dealcoholized, made up to 9 c.c. with water, and 1 c.c. of basic lead acetate is added. The precipitate is filtered off and the percentage of color removed is determined.

The results of these four tests on a number of commercial extracts are given in the following table. Plus (+) signifies a positive test for caramel, minus (—) a negative test. An interrogation mark (?) indicates some slight doubt as to the result obtained. A blank space signifies that there was not a sufficient amount of the sample available to make the test.

Of these samples 1, 6, 7, and 8 were known to be pure, and 17, 24, 25, 26, 28, and 29 acknowledged on the label the presence of caramel in the extract. Judging from the results obtained on these extracts, the lead acetate method and the extraction method as used here do not give reliable results. It is quite possible that the difficulty with the lead acetate method is the small volume and slight color of the final solution. Unfortunately, where other determinations need to be made on an extract, the amount available for the caramel test is usually too small to make possible much of an increase in the volume of the filtrate from the precipitate thrown down by the basic lead acetate. From the samples known to be pure, the minimum color removed was 96.2 per cent. If it is assumed that all samples giving a color removal as large as this or larger are free from caramel, then Extract 24 would

	Paraldehyde.	Phenyl-hydrazine.	"Color quotient."	Lead acetate.
				Per cent. color removed.
1	—	—	2.26	96.2
2	—	—	0.345	98.7
3	—	—	0.175	95.1
4	—	—	1.28	91.8
5	—	—	0.679	97.9
6	—?	—	1.86	99.2
7	—	—	1.04	88.3
8	—	—	0.934	97.5
9	—	—	1.49	99.0
10	—	—	0.322	97.0
11	—	—	2.06	98.2
12	—	—	1.62	96.8
13	—	—	1.24	. .
14	—	—	0.167	97.7
15	—?	—	. .	98.3
16	—	—	. .	97.1
17	. .	. .	1.21	95.8
18	+?	. .	1.74	96.2
19	+	+	0.799	97.6
20	—?	+	0.0	98.4
21	+	—	1.35	98.0
22	+	—	1.06	99.2
23	+	+	0.462	99.2
24	+	+	0.547	97.1
25	+	+	0.137	96.7
26	+	+	1.03	95.4
27	+	+	0.651	96.4
28	+	+	0.564	93.6
29	+	+	0.598	91.0
30	+	+	0.706	94.1
31	+	+	0.274	88.7
32	+	+	0.232	84.9
33	+	+	0.483	. .

be declared satisfactory, whereas it is admitted to contain caramel, and the other tests substantiate this statement. Many of the unknown samples, as well, show caramel by the other tests, but not by this one.

A consideration of the color quotients obtained with the extraction and absorption method shows this to be open to the same criticism as the basic lead acetate method. The minimum value obtained with the pure extracts is .934, whereas two of the adulterated extracts give quotients of 1.21 and 1.03, and so no figure can be established as the dividing line between pure extracts and extracts containing caramel.

The paraldehyde and phenyl-hydrazine tests as used here give results that agree with the facts of the case, and in the few instances where the result of one method is doubtful the accompanying test by the other method is sufficient to remove the doubt. The amount of sample required is only 15 c.c. and the use of a colorimeter is not necessary.

The procedure found to give the best results in this investigation and recommended for use is as follows: 15 c.c. of the extract are mixed with 2 c.c. of zinc chloride (5 per cent. solution), and 2 c.c. of caustic potash (2 per cent. solution) are added. The precipitate is filtered, washed with hot water, and dissolved in 15 c.c. of acetic acid (10 per cent. solution). This is concentrated to about half its volume, the excess acid neutralized, and the solution divided between two test tubes. To one of these three volumes of paraldehyde are added and just sufficient alcohol to make the mixture homogeneous. To the other tube an equal volume of a mixture of two parts phenyl-hydrazine hydrochloride, three parts sodium acetate, and twenty parts water is added. Both tubes will show a brown, flocculent precipitate after standing over night if caramel be present.

CONTRIBUTIONS FROM THE
RESEARCH LABORATORY OF PHYSICAL CHEMISTRY
No. 37

DETERMINATION OF THE HYDRATION OF IONS BY TRANSFERENCE EXPERIMENTS IN THE PRESENCE OF A NONELECTROLYTE[1]

BY EDWARD W. WASHBURN

I. PRINCIPLE OF THE METHOD

IF the transfer of electrolyte from one electrode to the other during a transference experiment is accompanied by a transfer of water, as would be the case if the ions are hydrated and carry water with them as they move through the solution, it is evidently possible to detect this transfer of water by having present in the solution a third constituent, which remains stationary during the passage of the current. By referring changes in content both of water and of electrolyte to this "reference-substance," the amounts of each transferred can be determined; and from these the "true"[2] transference numbers (T_i) can be calculated, and information in regard to the hydration of the ions derived.

II. REVIEW OF PREVIOUS INVESTIGATIONS

The first attempt to apply this principle was made by Nernst and his students.[3] In their experiments solutions of sulphuric, hydrochloric, hydrobromic, and nitric acids, containing boric acid as the reference-substance, were electrolyzed between platinum electrodes. The elec-

[1] This investigation was carried out with the aid of a grant made to Prof. A. A. Noyes by the Carnegie Institution of Washington.

[2] In the usual method of calculating transference numbers the assumption is made that the solvent is absolutely stationary; that is, that no transfer of solvent takes place from one electrode to the other. If such a transfer of solvent takes place, the calculation of the transference number by the ordinary method is not justified and will not give the *true transference number*, T_i. In fact, the number so obtained does not represent any physical quantity. Only in dilute solutions, where the amount of solvent transferred becomes negligible in comparison with the total solvent present, will the ordinary transference number, T_o, approach the true one, T_i.

[3] Nernst, Gerrard, and Oppermann, Nachr. Gesells. Wissensch., Göttingen, **56**, 86 (1900).

trode at which the concentration of the electrolyte increased was contained in a pipette placed in a beaker filled with the solution. The strong acid was determined by titration with 0.05 normal baryta solution, using methyl orange; and the boric acid, after the addition of mannite, was titrated similarly, using phenol phthalein. The errors involved in the analytical methods, amounting to from 0.2 to 0.3 per cent., render it impossible to draw any definite conclusion from their results, except that if water is transported at all under these conditions the amount is not very large.

Two years later Lobry de Bruyn[1] took up the problem. In his experiments a solution of silver nitrate containing methyl alcohol as the reference-substance was electrolyzed between silver electrodes in the "ordinary transference apparatus." The content in silver nitrate was determined by titration, and that in methyl alcohol by the distillation method. The author concludes that, "On peut facilement calculer que si l'ion Ag (ou l'ion NO_3) devait transporter, par example, une molécule du dissolvant, on trouverait pour une quantité de 4 grammes Ag à l'anode ou à la cathode respectivement une augmentation et une diminution, en eau de 0.6 à 0.7 gramme, ou en alcool méthylique de ± 1.2 grammes. L'analyse aurait montré qu'il en était ainsi, même si par diffusion les quantités avaient diminuées . . . ; il est donc à propos d'admettre que les ions . . . n'emportent pas le dissolvant avec eux, mais se meuvent seuls et libres." An examination of the experimental data does not justify this conclusion. Owing to the change in the boiling point of the solution with varying content of silver nitrate, the above mentioned change in composition might easily have escaped detection by the distillation method of analysis. Furthermore, the use of methyl alcohol as a reference-substance, especially in the high concentrations used by de Bruyn (24 to 64 per cent.), is open to grave objections, as will be explained below.

These two investigations constituted the only attempts which had been made to apply the method up to the time of the commencement of the present investigation.[2] During the progress of this investigation

[1] Lobry de Bruyn, Rec. trav. chim., **22**, 430 (1903).

[2] This investigation was begun in the latter part of 1904. In the earlier part of the investigation a molal sodium chloride solution was studied, using sugar (0.3 molal) as the reference-substance. The results of this part of the investigation, in which it was definitely shown that water was transported from anode to cathode during the electrolysis, were presented at a meeting of the Harvard-Technology Physico-Chemical Club, in May, 1905, and are recorded in the author's thesis of that year. (Mass. Inst. Tech., Chemical Theses, 1905.)

two other contributions to the problem have appeared. Morgan and Kanolt [1] attacked the problem, using solutions of silver nitrate in mixtures of alcohol and water. The analytical method for estimation of the alcohol content of the solutions before and after the electrolysis was considerably improved over the one used by de Bruyn, and every precaution was taken to prevent evaporation of the alcohol. As the experiments were intended to be qualitative only, the form of the apparatus was not adapted to quantitative experiments, since no middle portion was taken; and the electrolysis was prolonged, so that mixing of the electrode portions undoubtedly took place to some extent. The authors reasoned that "the best conditions for the detection of the combination of the water with the ions are found in a solution containing much less water than alcohol"; consequently they used solutions containing 53 per cent. and 66 per cent., respectively, of alcohol. Such a procedure is open, however, to serious objections. There is reason to believe [2] that in alcoholic solutions combination between this solvent and the ions also takes place, and if such is the case, the use of high concentrations of alcohol simply serves to complicate the problem. In fact, one essential condition should be that the concentration of the reference-substance in the solution be so small that its active mass shall be negligible in comparison with that of the solvent. Morgan and Kanolt were able to detect a change in the ratio of water to alcohol only in the 66 per cent. alcohol solution. In this case the change, while small, was probably outside the errors of experiment, and indicated that water was carried by the silver-ion or alcohol by the nitrate-ion, two possibilities of equal *a priori* probability between which it is impossible to distinguish.

The results of the three investigations just described left the question of hydration still an open one. To Gustav Buchböck [3] we owe the first successful application of the principle of this method. Working with solutions of hydrochloric acid and using mannite and resorcin at small concentrations as the reference-substances, he was able to prove that water is transported from the anode to the cathode during the electrolysis of these solutions. A satisfactory measurement of the amount transported was also obtained, the results at the two elec-

---

[1] Morgan and Kanolt, J. Am. Chem. Soc., **28**, 572 (1906).

[2] See Carrara, Ahrens' Sammlung, **12**, 413 (1908).

[3] Buchböck, Z. physik. Chem., **55**, 563 (1906).

trodes checking very well with each other. The results obtained with the two reference-substances are also nearly identical within the experimental error. His apparatus is shown in Figure 1. The two halves were connected by a ground glass joint at *b*, and the two stopcocks, *e* and *f*, permitted the separation of the solution into three parts at the completion of the electrolysis. The cathode was a small platinum wire sealed into the apparatus, and the anode (shown in cross-section) a torus made of the finest silver gauze. These two electrodes were enclosed between the wall and the short insert tubes, as shown. A diaphragm of silk gauze over the bottom of the insert tube on the cathode

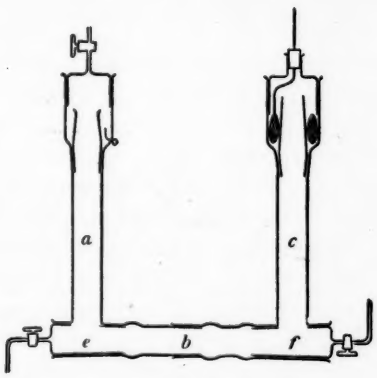

FIG. 1

side served to restrict the stirring caused by the evolution of hydrogen at this electrode.

The concentration of the hydrochloric acid was determined with an accuracy of a few hundredths of 1 per cent. by titration with an alkali solution free from carbonate in a weight burette, using phenol phthalein as the indicator. To determine the mannite, the solution, after neutralization with pure silver carbonate and removal of the excess of silver with hydrogen sulphide, was evaporated to dryness in a platinum dish and the mannite weighed directly. An accuracy of 0.05 to 0.10 per cent. was attained. In the experiments with resorcin as the reference-substance the content was determined by extracting the solution ten times with ether, evaporating the ethereal solution in a specially constructed apparatus, drying the residue in a current of hydrogen, and

weighing it directly. The accuracy was probably not better than 0.1 per cent.

In order to show that the reference-substance did not of itself migrate with the current, a regular transference experiment was made with a pure mannite solution in which 110 volts were applied to the electrodes for ten and a half hours. The silver coulometer showed a deposit of 0.004 gram of silver, and the analyses did not indicate any tendency on the part of the mannite to migrate with the current. The experimental data of Buchböck will be given and discussed later in connection with the results of the present investigation.

III. The Reference-Substance

The plan of the present investigation was to find a suitable material to use as a reference-substance, and then to measure the true transference numbers of the chlorides of the alkali metals and the quantity of water simultaneously transferred. Since the success or failure of this method depends almost entirely upon the properties of the reference-substance, this phase of the problem will first be discussed.

A satisfactory reference-substance must possess all of the following properties:

1. It must be a nonelectrolyte and must remain stationary with respect to the water when a current of electricity is passed through a solution containing it. This excludes all substances of a colloidal nature.

2. It must be a stable substance and must not react with or be acted upon by the electrodes, the solvent, the electrolyte, or any substance formed during the electrolysis.

3. Since the object of the investigation is to obtain information in regard to the state of hydration of the ions in *aqueous* solution, it is obvious that the reference-substance must be present at such a small concentration that it shall not appreciably change the character of the solvent.

4. Since, moreover, the changes in the ratio of water to reference-substance at the electrodes will be small, the reference-substance must be capable of very accurate estimation.

Since nearly all of the substances which fulfill the first of these conditions are organic compounds, and since such compounds do not fulfill the second condition in solutions of the alkali chlorides when they are electrolyzed between platinum electrodes, it became necessary,

first of all, to devise electrodes which could be used in these solutions without the appearance of oxygen or hydrogen, or the formation of acid or alkali, during the electrolysis. To meet this requirement the apparatus and electrodes described in a previous communication[1] were devised, and were used throughout this investigation. The silver anode and the silver chloride cathode prevented entirely the evolution of any gas or the formation of acid or alkali, and they had the further advantage of not introducing any foreign substance into the solution.

In choosing a reference-substance no compound was considered available unless its concentration in a 0.1 to 0.3 molal solution could be determined to 0.01 per cent. Three substances were found which fulfilled this condition, sucrose, raffinose, and arsenious acid. The final test of the availability of a compound for use as a reference-substance is its ability to remain entirely unchanged in the solution during an electrolysis with a current of 0.1 ampere for a period of at least fifteen hours. This final test is applied by making what is called a "straight tube run." This run differs in no way from the regular transference runs, except that it is made in a straight tube, with the silver anode at the top and the silver chloride cathode at the bottom. At the end of the run, instead of separating the solution into several portions, it is thoroughly mixed without opening the apparatus, and after the silver chloride has settled a portion of the solution is removed with a pipette and analyzed for the reference-substance. The substance is considered to be satisfactory if its concentration is the same (to 0.01 per cent.) at the end of this test as it was in the original solution. When the three substances mentioned above were subjected to this test only one of them, raffinose, was found to fulfill this condition rigorously. The results obtained with the other two are, therefore, only approximate. They will, however, be described, since they furnish checks on the order of magnitude and direction of transport of the water.

IV. Purification of Material

Sucrose. — The sucrose employed was a special unblued product, obtained directly from the refinery. It was further purified by three precipitations from water solution by the addition of pure alcohol. After washing with pure alcohol and ether, the crystals were dried at

[1] This Quarterly, **21**, 164 (1908).

95° and kept over calcium chloride. It had a specific rotatory power in 9.43 per cent. solution of $[\alpha]_D^{25°} = 66.410° \pm 0.0038$, and the specific conductance of the solution was less than 3.10^{-6} reciprocal ohms.

Raffinose. — This material was obtained from Kahlbaum, and was further purified by several recrystallizations from hot, pure methyl alcohol. The viscous mass which resulted from these crystallizations was dissolved in water and thrown out by diluting with pure ethyl alcohol. The beautifully crystalline product thus obtained was washed with alcohol and ether and dried at 50°.

Sodium Chloride. — This salt was prepared from Kahlbaum's product by precipitation with hydrochloric acid gas. After washing and drying, the salt was fused in platinum to ensure the removal of the last traces of hydrochloric acid.

Potassium Chloride. — Kahlbaum's product was recrystallized four times from conductivity water and the crystals fused in platinum. The salt gave a pure potassium flame.

Lithium Chloride. — Pure lithium carbonate was prepared from the commercial article by eight precipitations of the nitrate solution with pure ammonium carbonate, according to the method of Stas.[1] The resulting product was heated to 600° in an electric oven to remove ammonium salts. A solution of hydrochloric acid was prepared by expelling the gas from pure HCl solution (sp. gr. 1.20) with H_2SO_4 and receiving it in conductivity water. This solution was saturated with the lithium carbonate, and after filtering the filtrate was acidified with an excess of hydrochloric acid and evaporated to dryness. The lithium chloride thus obtained was dissolved to form a 1.3 molal solution. In order to make sure that the solution was exactly neutral it was tested with phenol phthalein, rosolic acid, and congo red, according to the method of Salm;[2] and the hydrogen-ion concentration was found to lie between the values 10^{-6} and 10^{-8}. The solution was consequently neutral, and it was used in preparing the solution for the lithium chloride experiments.

Arsenic Trioxide. — Kahlbaum's preparation was once resublimed and then twice recrystallized from hot water.

---

[1] Stas, Ouvres I, 689.

[2] Salm, Z. physik. Chem., 57, 500 (1907).

V. Preparation of Solutions

All the water used in preparing the solutions was conductivity water from the special still in this laboratory.[1] The raffinose and sugar solutions were prepared on the same day that the transference experiment was made, and were filtered through hardened filters to ensure the absolute clarity which is necessary for accurate polariscopic work. Just previous to filling the apparatus with the solution all dissolved oxygen was removed by boiling for five minutes at 30° under reduced pressure. All solutions were cooled to 2° above the dew-point whenever the transference of the solution from one vessel to another involved a possibility of a change in concentration due to evaporation.

In preparing the arsenious acid solutions, arsenic trioxide was dissolved in hot conductivity water and, after dilution to the proper concentration, the sodium chloride was added, and the whole solution was rotated for twenty-four hours at 25° in contact with a mixture of silver chloride and silver[2] to ensure equilibrium. Dissolved oxygen was removed by evacuation, and the solution was ready for use.

VI. Analytical Methods

Sucrose and Raffinose. — The concentrations of these two substances were determined by the optical method. This method, which is capable of a high degree of accuracy, has the further advantage that the whole of the electrode portion can also be used for the determination of the electrolyte, since the estimation of the carbohydrate does not affect the solution in any way when precautions are taken to prevent evaporation.

The polariscope used was a Schmidt and Haensch half-shade instrument of the Lippich type, the scale reading directly to tenths of a degree and the vernier directly to thousandths. The light was furnished by igniting sticks of fused sodium carbonate in an oxyhydrogen flame, and was further purified by filtration through a Landolt-Lippich ray filter. The instrument was kept in a dark room of even temperature, and was connected with a thermostat maintained at 25°, from which water was caused to circulate around the jacket of the 60-cm. polarizing tube. The average deviation of a set of six readings on this

[1] See Noyes and Coolidge, Proc. Am. Acad., 39, 190 (1903); Carnegie Inst. Pub., No. 63, 39 (1907).

[2] Such a mixture as is obtained from the cathode after a transference experiment.

instrument amounted to only 0.003° for a total rotation of 30°, thus permitting an accuracy of 0.01 per cent. in the reading. The same 60-cm. tube was used throughout this investigation. It was jacketed with a nickel-plated water jacket, and was provided with a thermometer in the side tube.

For the determination of the specific gravity of the solutions, pycnometers of the Ostwald-Sprengel type, having a capacity of 20 c.c.

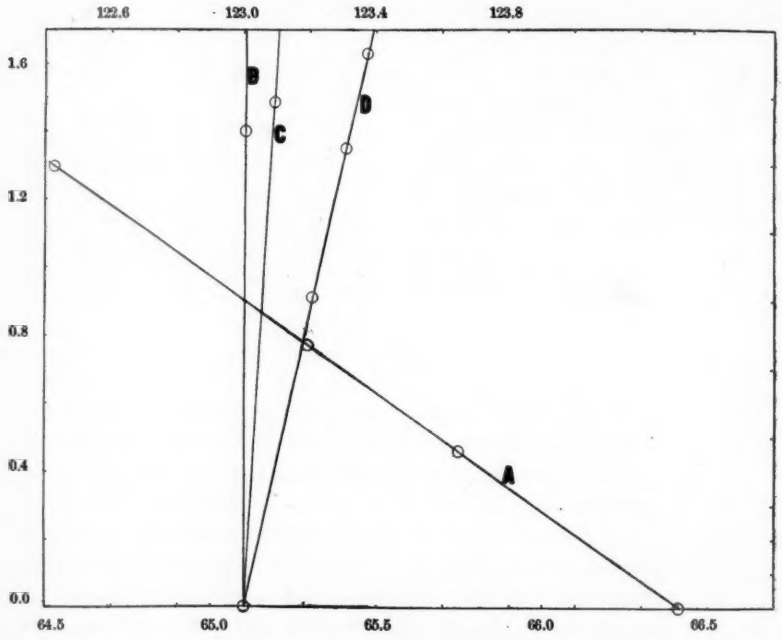

FIG. 2

and provided with ground glass caps, were used. (All specific gravities are at 25°, referred to water at 4°.) Air-free conductivity water was used in obtaining the water value of the pycnometer. A second pycnometer of the same type was used as a counterpoise, and all weights were reduced to vacuo. The error in the specific gravity determination never amounted to 0.01 per cent.

Effect of Salts on the Specific Rotatory Power. — Sodium chloride is known to reduce the specific rotatory power of cane sugar solutions,

the lowering depending upon the initial concentration of the sugar and being proportional to the amount of salt added.[1] It became necessary, therefore, to make a careful determination of this effect, so that corresponding corrections could be applied without introducing too large an error. The result of these determinations is shown in Figure 2, curve *A*. In this figure values of $[\alpha]_D^{25^\circ}$ are plotted as abscissæ (on lower line) and values of $\frac{P_s}{P_r}$ as ordinates, P_s representing the per cent. of salt (in this case NaCl) and P_r the per cent. of sugar in the solution, the ratio of sugar to water, $\frac{P_r}{P_w}$, being kept constant and in this case equal to 9.60. As is evident from this figure, the graph obtained is a perfectly straight line; its position, however, varies according to the ratio of sugar to water in the solution.

The effects of KCl, NaCl, and LiCl upon the specific rotatory power of raffinose were also investigated. A solution of raffinose, containing 0.1 formula-weight ($C_{18}H_{32}O_{16}$) per 1,000 grams of water, was employed. The results are given in the following table:

Salt.	Molal conc. of salt.	$[\alpha]_D^{25^\circ}$.
. . . . .	0.0	123.00°
KCl	1.3	123.08°
NaCl	1.71	123.12°
LiCl	1.30	123.24°

It is to be noted that the presence of the salts produces an increase in the specific rotatory power instead of a decrease, as in the case of sugar. The effect of LiCl was determined at three different concentrations and found to be linear. In none of the solutions, however, was it found necessary to apply any correction to the specific rotatory power of the raffinose due to the changes in the salt concentration at the electrodes, the correction being entirely negligible. Raffinose seems to possess the properties of an ideal reference-substance, being very

[1] See Muntz, Z. Ver. Zuckerind, **26**, 376 (1876), and Farnsteiner, Z. Ver. Zuckerind, **41**, 168 (1891).

stable in the apparatus and having a high specific rotatory power, which is not appreciably affected by changes in temperature or by changes in the concentration of the raffinose itself or of salts in the solution. The curves, showing the effects of these salts upon the specific rotatory power of raffinose, are also given in Figure 2. Curve *B* is for KCl, *C* for NaCl, and *D* for LiCl. Values of $[\alpha]_D^{25°}$ are plotted as abscissæ (upper line) and values of $\frac{P_s}{P_r}$ as ordinates.

Arsenious Acid. — This substance was estimated by titration with standard iodine solution, using disodium phosphate as the neutralizing agent. The details of this method, when an accuracy of 0.002 per cent. is required, have been described by the author in a previous paper.[1]

The Salts. — The chloride in the solution was determined by precipitating it from a weighed amount of the solution by means of an excess of a pure silver nitrate solution, and collecting and weighing the precipitate on a platinum Gooch crucible. The procedure was substantially that followed by Richards and Wells[2] in their "Revision of the Atomic Weights of Sodium and Chlorine." An accuracy of 0.01 per cent. was attained. The weights used in this investigation were carefully calibrated, and all weighings have been reduced to vacuo.

VII. Notation

$\alpha^{25°}$,	angular rotation of the plane of polarization by the solution at 25°.
$d^{25°}/_{4°}$,	specific gravity of the solution at 25° referred to water at 4°.
P_r,	per cent. of the reference-substance in the solution.
P_s,	per cent. of the electrolyte in the solution.
Ag^c,	grams of silver deposited in the coulometers.
m^e,	total mass in grams of the electrode portion.
Δm_w, Δn_w,	increase in grams (resp. mols) of water in the electrode portion.
Δm_s, Δn_s,	increase in grams (resp. mols) of electrolyte in the electrode portion.
$\mathcal{N}$,	equivalents of electricity passed through the solution.
T_t^c, T_t^a,	true transference number of the cation (resp. anion).
T_o^c, T_o^a,	ordinary transference number of the cation (resp. anion).

[1] J. Am. Chem. Soc., **30**, 31 (1908).

[2] Richards and Wells, Carnegie Inst. Pub., No. 28.

Δn_w^F, number of mols of water transferred from anode to cathode per faraday of electricity.

A, anode portion.

M_A, M, M_c, anode-middle, resp. middle, resp. cathode-middle portion.

C, cathode portion.

The most rational quantity to use in comparing the results at the two electrodes is the ratio of water transferred to salt transferred, *i. e.*, $\frac{\Delta n_w}{\Delta n_s}$, since this quantity depends only upon the analyses and is independent of the total weight of the electrode portion. This quantity will accordingly be inserted in the tables.

The final results of each experiment are most conveniently expressed by an equation which will be written in the two forms, A and B.

$$T_t^c N_w^c - T_t^a N_w^a = \Delta n_w^F. \tag{A}$$

$$N_w^c = \frac{\Delta n_w^F}{T_t^c} + \frac{T_t^a}{T_t^c} N_w^a. \tag{B}$$

In these equations N_w^c and N_w^a are the number of water molecules combined with one cation and one anion, respectively. The product of each of these quantities by the corresponding transference number is evidently the total amount of water carried by each ion when one equivalent of electricity passes through the solution, and the difference between these quantities represents the number of mols of water transferred from anode to cathode per faraday equivalent. Form B expresses the number of water molecules combined with the cation as an explicit function of the number combined with the anion. In this equation the constant, $\frac{\Delta n_w^F}{T_t^c}$, is evidently identical with the quantity, $\frac{\Delta n_w}{\Delta n_s}$. In using these general equations in the following sections, the superscripts, c and a, will be replaced by the symbol of the element in question in each case.

VIII. Data and Results with Sodium Chloride

Reference-Substance — Raffinose

Composition of solution:

Sodium chloride, 1.21 formula-weights of NaCl per 1,000 grams of water.

Raffinose, 0.1 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.

Applied E.M.F., 19 volts.
Current, 0.075 ampere
Duration of run, 12 hours.

TABLE I

	A.	M_A.	*M.*	M_c.	*C.*
$\alpha^{25°}$	34.99°	34.32°	34.33°	34.31°	33.80°
$d^{25°}/4°$	1.0495	. .	1.0608	. .	1.0705
P_r	4.584	. .	4.449	. .	4.341
P_s	4.731	. .	6.344	6.343	7.702
Ag^c	6.788	. .	. .	. .	6.787
m^c	78.13	. .	. .	. .	. .
Δm_w	—0.96	. .	. .	. .	. .
Δn_w	—0.53	. .	. .	. .	. .
Δm_s	—1.41	. .	. .	. .	. .
Δn_s	—0.0241	. .	. .	. .	. .
$\mathcal{N}$	—0.0629	. .	. .	. .	. .
$T_i^c = \frac{\Delta n_s}{\mathcal{N}}$	0.383	. .	. .	. .	. .
T_i^a	0.617	. .	. .	. .	. .
T_o^c	0.366	. .	. .	. .	.
T_o^a	0.634	. .	. .	. .	.
$\frac{\Delta n_w}{\Delta n_s}$	2.2	. .	. .	. .	2.0
n_w^E	0.84	. .	. .	. .	0.78

The data and results are shown in Table I. Owing to an uncertainty in the total weight of the cathode portion in this experiment, the transference number could not be obtained from this portion. The ratio of water to salt transferred, $\frac{\Delta n_w}{\Delta n_s}$, however, checks with the value obtained from the anode portion.

Reference-Substance — Sucrose

Several experiments were made with sodium chloride solutions, using sucrose as the reference-substance. In every case an increase in the concentration of the sugar at the anode and a corresponding decrease at the cathode were observed. Owing, however, to the uncertain stability of the sugar under the action of the electrode processes, the results were not very accurate from the quantitative standpoint. The best of these runs, with a 0.3-molal sugar solution, gave a value of the ratio, $\frac{\Delta n_w}{\Delta n_s} = 2$, at the anode and $\frac{\Delta n_w}{\Delta n_s} = 4$ at the cathode.

The low value of the conductivity of a pure sugar solution indicates the absence of any tendency on the part of the sugar to migrate under the influence of the E.M.F. However, in order to make sure that the presence of the sodium chloride is necessary in order to produce a concentration change at the electrodes when an electromotive force is applied for several hours to a sugar solution, the following experiment was made. A 10 per cent. sugar solution, containing 0.008 per cent. of sodium chloride, was placed in the regular transference apparatus, and a potential of 231 volts applied at the electrodes for the same length of time as in the regular transference runs. At the end of this time the solution in the neighborhood of each electrode was polarized, and the result was found to be identical with that given by the middle portion and by the original solution. It is thus evident that no concentration change takes place at the electrodes in the absence of the electrolyte, even with an electromotive force twelve times as great as in the regular runs.

Reference-Substance — Arsenious Acid

Arsenious acid did not prove to be a satisfactory reference-substance, owing to its uncertain stability during the passage of the current. One run, however, was obtained in which the arsenious acid had apparently undergone no oxidation at the electrodes, since the total amount present in the two electrode portions was equal to the amount present in the same weight of original solution. An increase of concentration was observed at the anode and a corresponding decrease at the cathode. The results are shown in the following table.

Composition of the solution:
Sodium chloride, 1.25 formula-weights of NaCl per 1,000 grams of water.
Arsenious acid, 0.20 formula-weight of H_3AsO_3 per 1,000 grams of water.

TABLE II

	Anode.	Cathode.
Ag^c	4.245	4.246
Δm_w	—0.35	0.36
Δn_w	—0.019	0.020
Δn_s	—0.0147	0.0149
$\mathcal{N}$	0.0393	0.0393
$T^c_s = \frac{\Delta n_s}{\mathcal{N}}$	0.374	0.379
$\frac{\Delta n_w}{\Delta n_s}$	1.3	1.3

Numerous attempts were made to repeat the results with arsenious acid, but without success, as check results at the two electrodes could not be obtained. A "straight tube run" showed a loss of arsenious acid, apparently due to oxidation. In view of this fact, the quantitative agreement of the results at the two electrodes, as shown in the above table, is to be regarded as more or less accidental, and the results are, therefore, chiefly of value as showing a concentration change in the same direction and of the same order of magnitude as in the case of sugar and raffinose.

Summary of the Results with Sodium Chloride

Three solutions of sodium chloride (1.2 molal), containing, respectively, as reference-substances, raffinose, sucrose, and arsenious acid, each at low concentration, were electrolyzed between reversible electrodes. In each case an increase in the concentration of the reference-substance was observed at the anode and a corresponding decrease at the cathode. If the assumption be made that the change in concentration is due to the transfer of water from anode to cathode during the electrolysis, the three experiments agree in showing that the ratio of mols of water

transported to mols of salt transported, $\frac{\Delta n_w}{\Delta n_s}$, lies between the values 1 and 4. The value obtained with raffinose is to be regarded as the most reliable value. The final values adopted for NaCl are given by the following equations:

$$0.383\, N_w^{Na^+} - 0.617\, N_w^{Cl^-} = 0.76 \pm 0.08,$$

$$\text{or} \quad N_w^{Na^+} = 2.0 \pm 0.2 + 1.61\, N_w^{Cl^-}.$$

IX. Data and Results with Potassium Chloride

Reference-Substance — Raffinose

Composition of solution:

Potassium chloride, 1.24 formula-weights of KCl per 1,000 grams of water.

Raffinose, 0.1 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.

Applied E.M.F., 19 volts.

Current, 0.096 ampere.

Duration of run, 14 hours.

	$C_{18}H_{32}O_{16}$	KCl
Total amount of solute in anode and cathode portions at completion of the run,	8.32 grams	15.27 grams
Total amount of solute in same weight of original solution,	8.33 grams	15.27 grams

The results are shown in Table III.

TABLE III

	A.	M_A.	*M.*	M_c.	*C.*
$\alpha^{25°}$	35.262°	34.827°	34.824°	34.825°	34.213°
$d^{25°}/_{4°}$	1.0578	1.0681	1.0681	. .	1.0807
P_r	4.516	. .	4.418	. .	4.290
P_s	6.510	8.105	8.108	8.108	10.030
Ag^c	5.3685	. .	. .	. .	5.3681
m^s	103.21	. .	. .	. .	85.280
Δm_w	—0.47	. .	. .	. .	0.61
Δn_w	—0.026	. .	. .	. .	0.034
Δm_s	—1.836	. .	. .	. .	1.839
Δn_s	—0.02460	. .	. .	. .	0.02465
$\mathcal{N}$	0.04974	. .	. .	. .	0.04974
$T_i^c = \frac{\Delta n_s}{\mathcal{N}}$	0.495	. .	. .	. .	0.495
T_i^a	0.505	. .	. .	. .	0.505
T_o^c	0.483	. .	. .	. .	0.481
T_o^a	0.517	. .	. .	. .	0.519
$\frac{\Delta n_w}{\Delta n_s}$	1.1	. .	. .	. .	1.4
n_w^E	0.52	. .	. .	. .	0.68

Summary of Results with Potassium Chloride

The direction of the concentration change is the same as with sodium chloride, but the amount of water transported is less. An especially noteworthy result is the value, 0.495, of the true transference number for the cation. *This is identical with the value obtained by Jahn,*[1] *at 25°, for KCl at infinite dilution, showing that the transference number for KCl is independent of the concentration up to 1.2 molal at least.* The value of the ordinary transference number at this concentration is 0.482, which illustrates the error introduced in transference

[1] Jahn, Z. physik. Chem., **58**, 645 (1907).

work if hydration is neglected. The final values adopted for KCl are shown in the following equations:[1]

$$0.495\, N_w^{K^+} - 0.505\, N_w^{Cl^-} = 0.60 \pm 0.08, \qquad \text{(A)}$$

$$\text{or} \quad N_w^{K^+} = (1.3 \pm 0.2) + 1.02\, N_w^{Cl^-}. \qquad \text{(B)}$$

X. Data and Results with Lithium Chloride

Reference-Substance — Raffinose

Composition of solution:

Lithium chloride, 1.28 formula-weights of LiCl per 1,000 grams of water.

Raffinose, 0.104 formula-weight of $C_{18}H_{32}O_{16}$ per 1,000 grams of water.

Applied E.M.F., 19 volts.

Current, 0.096 ampere.

Duration of run, 13 hours.

	$C_{18}H_{32}O_{16}$	LiCl
Total amount of solute in anode and cathode portions at the completion of the run,	8.78 grams	9.17 grams
Total amount of solute in same weight of original solution,	8.79 grams	9.18 grams

The results are shown in Table IV.

[1] In addition to the run with KCl and raffinose, a run with KCl and sucrose was also made, and an increase in the sucrose concentration at the anode and a corresponding decrease at the cathode were observed. The analyses were not completed, however, as quantitative results could not have been obtained without a careful investigation of the change in specific rotatory power of the sucrose, with varying concentrations of potassium chloride, and such an investigation did not seem worth while in view of the uncertain stability of the sugar during the electrolysis.

TABLE IV

	A.	M_A.	*M.*	M_C.	*C.*
$\alpha^{25°}$	37.045°	36.540°	36.558°	36.557°	35.819°
$d^{25°}/_{4°}$	1.0427	1.0454	1.0452	. .	1.0484
P_r	4.806	. .	4.730	. .	4.619
P_s	4.440	4.938	4.939	4.943	5.565
Ag^c	5.0116	. .	. .	. .	5.0112
m^e	104.4	. .	. .	. .	81.47
Δm_w	—1.1	. .	. .	. .	1.3
Δn_w	—0.62	. .	. .	. .	0.070
Δm_s	—0.604	. .	. .	. .	0.594
Δn_s	—0.0142	. .	. .	. .	0.0140
$\mathcal{N}$	0.04643	. .	. .	. .	0.04643
$T_t^c = \frac{\Delta n_s}{\mathcal{N}}$	0.306	. .	. .	. .	0.301
T_t^a	0.694	. .	. .	. .	0.699
T_o^c	0.278	. .	. .	. .	0.273
T_o^a	0.722	. .	. .	. .	0.727
$\frac{\Delta n_w}{\Delta n_s}$	4.3	. .	. .	. .	5.1
n_w^E	1.4	. .	. .	. .	1.6

Summary of the Results with Lithium Chloride

The concentration change is in the same direction as in the case of NaCl and KCl, but the amount of water transported is larger than with either of the other salts. The final values adopted for LiCl are shown by the following equations:

$$0.302\, N_w^{Li^+} - 0.698\, N_w^{Cl^-} = (1.5 \pm 0.1), \qquad \text{(A)}$$

$$\text{or} \quad N_w^{Li^+} = (4.7 \pm 0.4) + 2.29\, N_w^{Cl^-}. \qquad \text{(B)}$$

XI. Results with Hydrogen Chloride

TABLE V

Conc. reference-substance.	Conc. HCl.	T_t^c.			$\frac{\Delta n_w}{\Delta n_s}$.		
		Anode.	Cathode.	Mean.	Anode.	Cathode.	Mean.
Reference-Substance — Mannite							
0.135	1.0	0.844	0.844	0.844	0.30	0.28	0.29 ± 0.01
0.297	1.0	0.845	0.845	0.845	0.21	0.28	0.25 ± 0.03
0.141	1.47	0.836	0.840	0.838	0.33	0.34	0.33 ± 0.01
0.353	1.47	0.844	0.844	0.844	0.25	0.24	0.24 ± 0.02
0.353	1.47	0.843	0.844	0.844	0.22	0.26	
0.717	1.47	0.845	0.847	0.846	0.21	0.23	0.22 ± 0.01
Reference-Substance — Resorcin							
0.214	1.1	0.840	0.842	0.841	0.29	0.39	0.34 ± 0.05
0.408	1.1	0.843	0.842	0.842	0.38	0.34	0.36 ± 0.02
1.07	1.1	0.845	0.844	0.845	0.46	0.39	0.42
1.98	1.1	0.845	0.844	0.844	0.49	0.41	0.45
0.328	3.07	0.839	0.840	0.840	0.40	0.41	0.41
0.636	3.07	0.837	0.838	0.837	0.43	0.39	0.41
1.31	3.07	0.839	0.838	0.839	0.47	0.47	0.47

The results obtained by Buchböck have been recalculated so as to show the values of $\frac{\Delta n_w}{\Delta n_s}$ and of T_t^c, obtained at each electrode.[1] These values are shown in Table V, concentrations being expressed in formula-weights per 1,000 grams of water. The excellent agreement of the results at the two electrodes attests the high degree of accuracy which

[1] Buchböck apparently did not make use of the total number of equivalents of electricity passed through the solution, as shown by his coulometer. The values of T_t given by him are, therefore, the means of the two values which can be obtained from each electrode separately. He gives, also, only the change in the number of *grams* of water at each electrode, a quantity which is dependent upon the total weight of the electrode portion and which is more liable to be affected by any error arising from admixture with the middle portion than is the value of $\frac{\Delta n_w}{\Delta n_s}$. I have accordingly computed values of T_t^c and of $\frac{\Delta n_w}{\Delta n_s}$ for each electrode from his original data.

this investigator was able to attain in his analyses. In fact, only two criticisms of the experimental part of the work can be made: (1) the failure to maintain a constant temperature by use of a thermostat, and (2) the analysis of only one middle portion. In regard to the first of these, the author does not record the temperature at which his experiments were carried out, but simply makes the statement: "Ein grosser Teil der Unsicherheiten . . . mag übrigens darauf zurückzuführen sein, dass die Temperatur bei diesen Versuchen nicht berücksichtigt wurde, . . . so kann zwischen einzeln, differenz von etwa 10° bestanden haben, was auf die Resultäte nicht einflusslos geblieben sein durfte." The necessity for analyzing more than one middle portion in transference work has already been discussed.[1]

An examination of the results obtained with mannite leads to the conclusion that the value of $\frac{\Delta n_w}{\Delta n_s}$ is independent (within the experimental error) of the concentration of the mannite up to 0.4 molal, and of the concentration of the hydrochloric acid up to 1.5 molal. The same conclusion holds for the results obtained with resorcin, but the value seems to be somewhat higher. This may be due, as the author suggests, to a combination of some of the resorcin with the ions, and the more or less progressive change with the concentration of the resorcin at the higher concentrations would seem to support this view. In view, however, of the uncertainty with respect to the temperature and of the fact that the results obtained with resorcin are probably not so accurate as those obtained with mannite, it seems best to adopt the value, $\frac{\Delta n_w}{\Delta n_s} = 0.28 \pm 0.04$, as the most probable one. The most probable values of the transference numbers are, similarly, $T_i^c = 0.844$, $T_i^a = 0.156$.[2]

[1] See previous communication, this QUARTERLY, 21, 175 (1908).

[2] Buchböck treats his result in a somewhat different manner. Using the means, he extrapolates his hydration values to zero concentration, both of the hydrochloric acid and of the reference-substance. Although, as the table indicates, there seems to be a somewhat regular change in the mean hydration values, $\frac{\Delta n_w^E}{T_i^a}$, with the concentration, an extrapolation to infinite dilution seems not to be exactly warranted, in view of the variations in the values obtained at the two electrodes. It seems better to adopt a mean value from the data for the more dilute solutions and to conclude that, in moderate concentrations of HCl (up to, say, 1.5 molal) and with the concentration of the reference-substance so small that it does not appreciably change the activity of the water (say up to 0.3 molal), the results obtained both for transference number and for relative hydration are independent of the concentration of both electrolyte and reference-substance within the experimental errors.

The final values adopted for HCl are given by the following equations:

$$0.844\,N_w^{H^+} - 0.156\,N_w^{Cl^-} = 0.24 \pm 0.04,$$

$$\text{or} \quad N_w^{H^+} = (0.28 \pm 0.04) + 0.185\,N_w^{Cl^-}.$$

XII. Discussion of the Results

The *facts* which have been thus far established may be stated thus: *The electrolysis of a solution of potassium, sodium, or lithium chloride, or of hydrochloric acid, containing a nonelectrolyte at low concentration, is attended by an increase in the concentration of the nonelectrolyte at the anode and a corresponding decrease at the cathode, but no change in concentration takes place in the absence of the electrolyte.* These results are open to but two possible interpretations: (1) the reference-substance is carried by the electrolyte from cathode to anode, or (2) water is carried by the electrolyte from anode to cathode during the passage of the current.

The former hypothesis involves the assumption of the formation of a complex between the reference-substance and the chloride-ion in each case. This assumption alone is not sufficient, however, since it requires that the result obtained shall depend only upon the concentration of the chloride-ion, and shall be independent of the nature of the cation. The experiments with raffinose in solutions of potassium, sodium, and lithium chlorides show that this is not at all the case. In order that the first hypothesis shall explain the results, it is therefore necessary to assume, not only the formation of a complex with the chloride-ion in each case, but also the formation, but to a less degree, of a complex with the cation, the amount of the latter complex varying with the nature of the cation and increasing in the series Li, Na, K. This involves, moreover, in the case of sodium chloride, the assumption of the same kind and degree of complex formation with the ions in solutions containing substances of such highly different character as raffinose and arsenious acid. Similarly, in the case of hydrochloric acid, the two very different substances, mannite and resorcin, must unite practically in the same way with the ions of hydrochloric acid in order to explain the facts according to the first hypothesis. Moreover, Buchböck's experiments show that an increase of *300 per cent.* in the concentration of the nonelectrolyte or of *50 per cent.* in the concentration of the hydrochloric acid is without

appreciable influence upon the results, which obviously could not be the case if the ions were forming complexes with the nonelectrolyte.

In order to explain by this hypothesis the concentration changes resulting when a solution of potassium chloride containing sucrose is electrolyzed, it is necessary to assume that more sucrose is combined with chloride-ion than with potassium-ion. This state of things might result in two ways, as shown by the following equilibria:

$$\begin{aligned} C_{12}H_{22}O_{11} \quad &+ K^+ = [K(C_{12}H_{22}O_{11})]^+ \\ C_{12}H_{22}O_{11} \quad &+ Cl^- = [Cl(C_{12}H_{22}O_{11})]^- \end{aligned} \qquad (1)$$

$$\begin{aligned} x(C_{12}H_{22}O_{11}) &+ K^+ = [K(C_{12}H_{22}O_{11})_x]^+ \\ y(C_{12}H_{22}O_{11}) &+ Cl^- = [Cl(C_{12}H_{22}O_{11})_y]^- \end{aligned} \qquad (2)$$

In the first case we must assume that more of the chloride-ion-sucrose complex is formed than of the potassium-ion-sucrose complex. In the second case we must assume that y is greater than x, and sufficiently greater to give always more sugar in combination with the chloride-ion. In either case, application of the Mass-Action Law shows that increasing the concentration of the sugar will affect the two equilibria differently, the chloride-ion complex increasing at a more rapid rate than the potassium-ion complex. The mobilities of the two ions will, therefore, not change at the same rate, and the conductivity of a potassium chloride solution with varying concentrations of sucrose in the solution should be some other function than a linear one. The accompanying plot (Fig. 3), obtained by Masson and Martin,[1] shows no indication of any such combination of sucrose with the ions, the effect of the presence of the sucrose being simply to increase the viscosity of the medium and slow up both ions. In this figure, in which the curve for hydrochloric acid is also given, values of the equivalent conductivity, λ, are plotted as abscissæ and molal concentration of sucrose as ordinates.

The first hypothesis may therefore be considered as eliminated so far as any considerable effect is concerned.[2] The results obtained must, therefore, be due to the migration of water with the current; and, since the presence of the electrolyte is necessary to produce the result, we must assume some sort of a complex between the water and one or

[1] Masson and Martin, J. Chem. Soc., 79, 707 (1901).

[2] It is, of course, possible that the numerical values obtained are affected to some extent by a slight tendency on the part of the reference-substance to combine with the ions. Such an effect, if present at all, is probably very small, however. This is readily understood, since the active mass of the reference-substance is very small compared with that of the water (about 1 to 500).

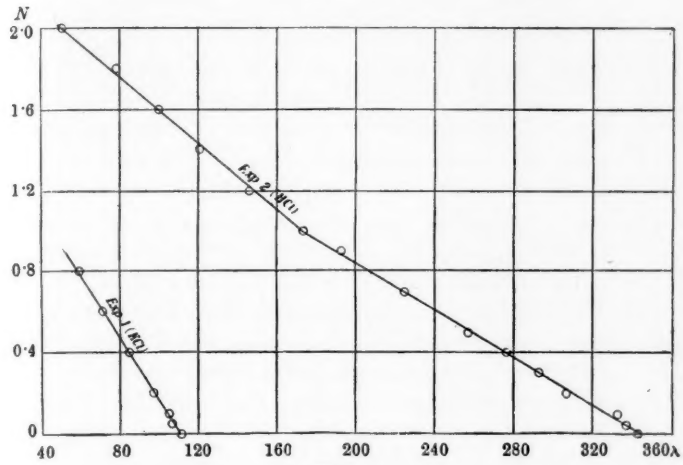

FIG. 3

both ions in each solution. This assumption is entirely in accord with all the results, and moreover serves to explain a number of facts in connection with the Ionic Theory which would otherwise be difficult to understand.[1]

Let us now consider the results as interpreted quantitatively upon the basis that the reference-substance does not migrate at all during the passage of the current. The results presented above for all the different electrolytes are collected in Table VI.

TABLE VI[1]

Electrolyte. Conc. 1 to 1.5 *M.*	$\frac{\triangle n_w^F}{T_t^c}$.	$\triangle n_w^F$.	$T_{t^+}^c$	$T_{=}^c$.	$T_{c^-}^c$
HCl	0.28 ± 0.04	0.24 ± 0.04	0.844	0.83	0.82
KCl	1.3 ± 0.2	0.60 ± 0.08	0.495	0.495	0.482
NaCl	2.0 ± 0.2	0.76 ± 0.08	0.383	0.396	0.366
LiCl	4.7 ± 0.4	1.5 ± 0.1	0.304	0.330	0.278

[1] In this table, as well as in previous instances, the values given are the *means* of the two results obtained from each electrode independently. The deviation of this mean from the two individual values is indicated in each instance. Since most of the errors peculiar to transference experiments have a tendency to make the changes at the electrodes smaller in magnitude, if anything, than they should be, the deviations indicated may be considered as a fairly reliable measure of the maximum error of the results.

[1] For a full discussion of these facts in relation to the general problem of hydrates in solution, see Washburn, "Hydrates in Solution: A Critical Review of Recent Experimental and Theoretical Contributions to this Problem." Jahrb. Rad. u. Elec., December, 1908.

$$N_w^{H^+} = 0.28 \pm 0.04 + 0.185\, N_w^{Cl^-}. \quad (1)$$

$$N_w^{K^+} = 1.3 \pm 0.2 + 1.02\, N_w^{Cl^-}. \quad (2)$$

$$N_w^{Na^+} = 2 \pm 0.2 + 1.61\, N_w^{Cl^-}. \quad (3)$$

$$N_w^{Li^+} = 4.7 \pm 0.4 + 2.29\, N_w^{Cl^-}. \quad (4)$$

Absolute Hydration of the Ions

From the above equations, which give a relation between the hydration of the separate ions of each salt, the absolute hydration could be calculated if the value were known for any one ion. In Table VII the number of molecules of water combined with each ion is given for different assumptions regarding the number combined with the chloride-ion.

TABLE VII

MOLS OF WATER COMBINED WITH ONE MOL OF EACH ION

Cl^-.	H^+.	K^+.	Na^+.	Li^+.
0	0.28	1.3	2.0	4.7
1	0.46	2.3	3.6	7.0
2	0.65	3.3	5.2	9.3
3	0.83	4.3	6.8	11.6
4	1.02	5.4	8.4	13.9
5	1.2	6.4	10.0	16.2
6	1.4	7.4	11.6	18.5
7	1.6	8.4	13.2	20.8
8	1.8	9.5	14.9	23.1
9	2.0	10.5	16.6	25.3
10	2.1	11.5	18.0	27.6
11	2.3	12.5	19.4	30.2
12	2.5	13.5	21.3	32.2
20	5.0	21.7	34.2	50.5
. .	$\pm$ 0.04	$\pm$ 0.2	$\pm$ 0.2	$\pm$ 0.4

A glance at this table shows several interesting facts. The first row of figures evidently represents minimum values, since a negative hydration for the chloride-ion would have no meaning. The last row represents impossible values, since it requires that in a solution containing 1.2 mols of LiCl per 1,000 grams of water, approximately 70 mols of water must be combined with the two ions. Since such a solution contains only 55.5 mols of water altogether, the assumption of 20 mols of water on the chloride-ion is incorrect. Even the assumption of 12 mols of water combined with each mol of chloride-ion leads to the necessity of assuming that 44 out of a total of 55 mols of water is in combination with the ions, to say nothing of the amount in combination with the undissociated molecules. We may, at any rate, safely conclude that this row gives us maximum values.[1] It is therefore clear that all the cations in question are hydrated, that all those of the alkali elements are more hydrated than the chloride-ion, and that the hydration increases markedly between each successive member of the series, hydrogen, potassium, sodium, lithium.

Relations between the Hydration and the Conductance of Ions

The remarkable fact early attracted attention that in the case of elementary ions of any one group of the periodic system, those of smaller atomic weight possess a lower equivalent conductance, and therefore a smaller migration velocity. As a plausible explanation of this fact, it has been suggested[2] that the ions of the lighter elements are more hydrated (and therefore really larger and heavier) than those of the

[1] In order to decide which set of values to adopt, it is necessary to know some other relation between the hydration of the ions for some one of the above substances. As explained by the author in another place (*loc. cit.*, Jahrb. Rad. u. Elec.), if accurate data were available on the lowering of the vapor pressure at 25°, of say 0.5 molal solution of the above chlorides, a fair idea of the *total* amount of water in combination might possibly be obtained; and once this is known for any one salt, approximate values for the absolute hydration of all the above ions could be calculated. Vapor pressure data on several of the above chlorides would also make it possible to test the assumptions, since if these are correct the same values for the hydration of the ions should be obtained from the lowering of vapor pressure for each salt. It is to be hoped that such data will soon be available. It is, of course, possible to calculate the vapor pressure lowering at 25° from the data on the lowering of the freezing point if the heats of dilution are known. Data on the lowering of the freezing point and heat of dilution are available but are of doubtful accuracy, and it has not, therefore, seemed advisable to attempt the calculation of the total amount of combined water until accurate data are available. From the data at present available, we should conclude that the true values lie somewhere in the first six rows of Table VII.

[2] Bredig, Z. physik. Chem., 13, 277, No. 2 (1894); Euler, Wied. Ann., 63, 273 (1897); Kohlrausch, Proc. Roy. Soc., 71, 338 (1901).

heavier elements. This explanation has now for the first time, by the results of this research, received conclusive confirmation.

Table VIII contains comparative data for the three alkali elements investigated. The second column contains the atomic weight of the element; the third, its atomic volume in the solid state; the fourth, the equivalent conductance of its ion at 18° as derived by Kohlrausch; the fifth, a formula representing the minimum hydration consistent with the transference results (see first row of Table VII); the sixth, the corresponding molecular weight of this hydrated ion; and the last two columns, the apparent molecular volume of the chloride in solution, calculated from density data[1] by the hypothetical principle that the uncombined water in the solution has the same volume as an equal quantity of pure water at the same temperature, and under the special assumptions, first (under I), that none of the water is combined, and second (under II), that the quantity combined is that which corresponds to the minimum formulæ in the sixth column (chloride-ion being thereby assumed anhydrous).

TABLE VIII

Element.	At. wt.	At. vol.	Equiv. cond.	Formula of hydrated ion.	Mol. wt. of hydrated ion.	Apparent Mol. Vol. of Chloride in Solution.	
						I.	II.
Potassium	39.1	45.5	64.6	$K(H_2O)_{1.3}$	62.5	26.4	49.8
Sodium	23.0	23.7	43.5	$Na(H_2O)_{2.0}$	59.0	16.8	52.8
Lithium	7.0	13.1	33.4	$Li(H_2O)_{4.7}$	92.0	16.0	100.5

If a larger hydration be assumed (for example, that corresponding to 2 mols of water on the chloride-ion), the differences in the molecular weights of the ions and the molecular volumes in solution of the chlorides become still more pronounced.[2]

[1] See Ruppin, Z. physik. Chem., **14**, 482 (1894); also Forch, Ann. Phys., **12**, 591 (1903).

[2] In the above calculations of the apparent molecular volumes in solution, the assumption is made that the uncombined water in the solution has the same volume as in the pure state. This is probably not the case, as changes in the complexity of the water are also accompanied by changes in volume. Such changes would, however, probably be of the same order of magnitude in each of the above cases, so that the apparent molecular volumes in solution, thus calculated, for salts of one group, may still properly be used for purposes of comparison with one another. The values are for 0.25 molal solutions at 25°.

The present investigation has shown further that the values which have heretofore been obtained for the transference numbers of many, if not all, electrolytes in concentrated solutions by the Hittorf method are to be regarded as erroneous, since their calculation involves the assumption that the solvent remains stationary during the electrolysis. A glance at Table VI shows the error produced in the transference number by neglecting hydration. In the case of potassium chloride, instead of decreasing from 0.495 at infinite dilution to 0.482 at 1.2 molal, as heretofore assumed, the transference number is found to remain unchanged over this range of concentration. This is in entire agreement with the fact that the mobilities of the potassium and chloride-ions are very nearly the same, and consequently a change in the viscosity of the medium should affect the velocities of both ions about equally.

In the case of the other ions the change of the transference number with the concentration is much less than has heretofore been assumed. Thus in the case of sodium chloride it is from 0.396 to 0.383 instead of to 0.366; in the case of lithium chloride from 0.330 to 0.304 instead of to 0.278.

XIII. The Relation between the True and the Ordinary Transference Numbers

We have seen that the ordinary transference number (T_o) for concentrated solutions, as obtained by the Hittorf method, is erroneous in cases where the ions are hydrated, since it is calculated on the assumption that the water remains stationary during the passage of the current. A relation, however, exists between the quantity so calculated (T_o), the true transference number (T_t), and the number of mols of water (Δn_w^E) transferred per equivalent of electricity. The derivation of this relation will be readily understood from the following considerations. Let one equivalent of electricity be passed, for example, through a potassium chloride solution with a silver anode and silver chloride cathode. As a result, T_t^c equivalents of KCl and Δn_w^E equivalents of water are transferred from anode to cathode. As a result of the water transference, the ratio of salt to water at the cathode is not so great as it would be if no water were transferred. Consequently, if the whole concentration change be attributed to the transfer of salt alone, the number of mols of salt transferred by the current will appear smaller than it really is. It should be increased by the amount of salt originally associated with

the water transferred. This amount is obviously the quantity, $\Delta n_w^F \frac{n_s}{n_w}$, where $\frac{n_s}{n_w}$ is the ratio of mols of salt to mols of water in the original solution. When this correction is made we obtain the relation,

$$T_t^c - T_o^c = \Delta n_w^F \frac{n_s}{n_w}.$$

This is an important equation; for, since the ordinary transference number (T_o) is usually known or can be determined experimentally by the Hittorf method, this equation offers a means of calculating either the true transference number (T_t), or the water transference (Δn_w^F), provided the other is known. By the method of the present investigation all three quantities are directly measured. Other methods are available, however, which give the value of either T_t or Δn_w^F alone.

Lewis[1] has recently described a method for obtaining the quantity, Δn_w^F. The principle of this method consists in measuring the potential of a concentration cell, both solutions of which are saturated with the electrolyte, the latter being only sufficiently soluble to form a dilute solution. One of the solutions, however, contains in addition a certain amount of some nonelectrolyte, so that the vapor pressure of the water is different on the two sides of the cell. If the nonelectrolyte does not combine with the ions, the only change attending the operation of such a cell would be the transfer of water from one solution to the other. The potential of the cell would therefore be a direct measure of the work done in transferring the water; and the amount so transferred (Δn_w^F) could be calculated from the relation of this work to the known work involved in transferring one mol of water from a solution with one vapor pressure to a solution with another vapor pressure. This method is now being applied experimentally in this laboratory.

It has been shown by Mr. R. C. Tolman, who is now investigating it in this laboratory, that the centrifugal method of des Coudres[2] gives directly the true transference number. In this method a solution of the electrolyte is placed in the tube of a centrifugal apparatus and rotated at a high speed. As a result of the unequal mobilities and densities of the two ions, an electromotive force is set up between the

[1] Lewis, Z. Electrochem., **14** (1908); J. Am. Chem. Soc., **30**, 1355 (1908).

[2] Wied. Ann., **49**, 284 (1883). See also his gravitation method involving the same principles, *ibid.*, **57**, 232 (1896).

inner and outer ends of the tube and can be measured by the use of suitable electrodes. From the principles of thermodynamics an equation can be derived connecting this electromotive force with the speed of rotation, the distances of the inner and outer electrodes from the centre of rotation, the partial volume of the electrolyte and of the electrode material in the solution, and the true transference number. Since all the other quantities are capable of measurement, the true transference number can be calculated. No sufficiently accurate data are yet available, however.

Another method for obtaining the true transference number is the method of moving boundaries. This method has recently been so perfected by Denison and Steele[1] as to equal in accuracy the Hittorf method. In dilute solution the true transference number and the ordinary one as obtained by the Hittorf method are identical, as is evident by referring to the equation connecting them (since the ratio $\frac{n_s}{n_w}$ is then very small). Denison and Steele found, in fact, that all their results for dilute solutions agreed satisfactorily with those obtained by the Hittorf method. In concentrated solutions, however, large deviations were observed, which these investigators were unable to explain. Thus, they remark: "Wir haben die Messungen öfters widerholt, aber immer mit demselben Resultat, und zwar 0.508 bis 0.510 für die Anionüberführungszahl von 1.0-norm. KCl und 0.613 bis 0.615 für 1.0-norm. NaCl. Die allgemein angenommenen Werte dieser Grössen sind etwa 0.514 für 1.0-norm. KCl und 0.63 für 1.0-norm. NaCl. Der Grund dieser Abweichung muss vorläufig dahingestellt bleiben; für unsern Zweck genügt es aber, dass schon in 0.1-norm. Lösungen der Unterschied zwischen unsern Zahlen und den durch die analytische Methode gelieferten nicht mehr besteht."

The explanation for this difference between the values obtained by Denison and Steele and the Hittorf values is now apparent: *The rate of motion of the ion-boundary through the solution is a direct measure of the true transference number*[2]; consequently, the results obtained

[1] Denison and Steele, Z. physik. Chem., 57, 110 (1906).

[2] It is true that when the motion of the boundary is measured, as in the experiments of Denison and Steele, by means of a reference point outside of the solution, any displacement of the solution as a whole through volume changes accompanying the electrode processes would affect the apparent rate of motion of the boundary. The authors state, however, that in the case of their experiments, there was not an appreciable change of volume as a result of the electrode process.

by this method should differ from those obtained by the Hittorf method for concentrated solutions. It is therefore interesting to compare the results obtained by Denison and Steele with the values obtained in the present investigation. These are brought together in the following table (Table IX). The values are those for the cation.

TABLE IX

	True Transference Number.		Ordinary Transference Number.
Salt.	Denison and Steele.	Washburn.	Washburn.
KCl	0.492 [1]	0.495 [2]	0.482
NaCl	0.386 [1]	0.383 [2]	0.366

[1] For a molal solution at 18°. [2] For a 1.25 molal solution at 25°.

When the difference in temperature and concentration is considered the agreement seems to be satisfactory.[1] Denison and Steele also obtained the same transference number for molal and for 0.1 molal potassium chloride solutions, which agrees perfectly with the result of the present investigation.

By measuring true transference numbers by the method of moving boundaries and "ordinary" transference numbers by the Hittorf method, it is obvious that we are in possession of an excellent method for determining the relative degrees of hydration of the ions, a method which does not require the presence of any third constituent in the solution and which is free from all arbitrary assumptions. Future investigations in this direction seem to offer the most promising line of attack upon the problem of hydration in solutions of electrolytes.

XIV. Summary

1. This investigation has shown that the electrolysis of a solution of potassium, sodium, or lithium chloride, containing a nonelectrolyte at low concentration, is attended by an increase in the ratio of the quantity of nonelectrolyte to that of the water at the anode and by a correspond-

[1] Denison and Steele found that the values they obtained for concentrated solutions varied somewhat with the nature of the "indicator salt," so that the method must be pursued further, experimentally, before a final decision can be arrived at regarding the correct values for concentrated solutions.

ing decrease at the cathode, but that no change takes place in this ratio in the absence of the salt.

2. It is shown that this change is to be attributed mainly, if not wholly, to a transfer of water from the anode to the cathode during the electrolysis.

3. By referring the changes in the content of water and of salt to the nonelectrolyte as a reference-substance, a relation between the degrees of hydration of the chloride-ion, the lithium-ion, sodium-ion, and potassium-ion has been derived. A similar relation involving the hydrogen-ion had been previously obtained by Buchböck.

4. The results show that all these cations are hydrated; that the hydration increases markedly between each two members of the series H^+, K^+, Na^+, Li^+; and that the smallest values of the hydration consistent with the data are represented by the formulæ: $[H(H_2O)_{0.3}]^+$, $[K(H_2O)_{1.3}]^+$, $[Na(H_2O)_{2.0}]^+$, and $[Li(H_2O)_{4.7}]^+$. The hydration of all these ions may, however, be considerably greater than these values.

The fact that the ions of the elements of a group of the periodic system increase in migration velocity with increasing atomic weight has heretofore been explained by assuming that the ions of the lighter elements are more highly hydrated. The correctness of this explanation has been demonstrated by the results of this research.

5. It is further shown that, owing to the transfer of water during the electrolysis, the transference numbers hitherto obtained for the more concentrated solutions of these chlorides are erroneous, since the calculation involved the assumption that the water remained stationary. The true transference numbers, derived by reference to the nonelectrolyte, are found to vary with the concentration much less than the apparent ones previously computed. In the case of potassium chloride, there is no variation whatever up to a concentration of 1.2 molal.

6. A mathematical relation between the true transference number and the ordinary one as obtained by the Hittorf method is derived. It is also pointed out that the method of moving boundaries gives the true transference number. The results of Denison and Steele obtained by this method are compared with the true transference numbers obtained in the present investigation and shown to agree. Attention is called to the fact that the combination of transference numbers obtained by the Hittorf method with those obtained by the method of moving boundaries furnishes a very promising method for further investigating the hydration of ions.

In conclusion, I desire to express my great indebtedness to Professor A. A. Noyes, whose interest, coöperation, and encouragement throughout the progress of this investigation have made possible its successful completion.

To the Carnegie Institution of Washington, whose financial assistance has made possible the continued prosecution of the research, grateful acknowledgments are also due.

BOSTON, MASS., July 1, 1908.

CONTRIBUTIONS FROM THE
LABORATORY OF SANITARY CHEMISTRY

METHODS OF TESTING THE EFFICIENCY OF VENTILATION

BY ELLEN H. RICHARDS, E. MARION WADE, ROYCE W. GILBERT,
CARL E. HANSON, JAMES M. TALBOT

THE application of scientific knowledge to the daily living conditions of human beings is demanded today as never before. We are slowly learning that these applications may be made without, in all cases, using the time-consuming methods of exact science. It is a working basis for the betterment of conditions that is demanded, and a more general use of the facts as fast as learned.

Especially is this true of the examination of the air supply of rooms, shops, dining halls, and places of amusement and of study.

The general quality of the air is in question. Is it fit for human beings to breathe? The facts brought out in the course of the crusade against tuberculosis show that in a far too large number of circumstances the general conditions are dangerous, and that a concerted effort must be made to interest the people to better them.

To secure these general facts in a sufficient number of cases requires methods which shall be reliable and accurate within limits, and not so time-consuming as to be prohibitive.

A systematic effort has been made to meet this want by the classes studying Air Analysis at the Institute of Technology; namely, Course II, Mechanical Engineering, Option 4; Course V, Chemistry; Course VII, Biology; and Course IX, Sanitary Engineering. Some results of the past two years' experience are here given.

A general consensus of opinion among recent investigators points to recorded temperature as the most practicable means of controlling ventilation under modern conditions. The temperature of any given room may increase by any one or any combination of the following causes: (1) Heat given off by the bodies of the occupants and by their breath;

(2) Heat given off by the lights; (3) Rise of outside temperature; and (4) An excess of heat from the heating plant.

The last of these causes should be practically eliminated in a modern, well-constructed, and well-managed public structure. Of course the average private home has not yet reached this point of refinement in the perfection of its heating system, but it is not the small individual house or even the apartment house that is usually in need of ventilation. In a small room with few occupants, the doors, windows, and cracks usually provide sufficient change of air. It is in the large halls, office buildings, schools, etc., where many persons are congregated under one roof, that ventilation is most needed and inspection of ventilation is most important. In all such places the heating system is, or should be, designed to deliver a constant amount of heat for any given period of time.

Contrary to the old theory that a heating plant should "keep a room at a given temperature," and so automatically supply less and less heat as the heat derived from the occupants increases, the new idea is rather that the plant deliver a constant predetermined amount and that the ventilating plant keep the room at the desired temperature. This idea is really carried out in most of the buildings with which the ventilating engineer or inspector would have to deal. This being the case, any rise of temperature in a room would be caused by the animal heat of the occupants, effect of the lights, or by rise of the outside temperature. This last cause is slight in any instance and may usually be neglected.

Then, since in giving off heat the body and the lights (with the exception of electric incandescent) give off both CO_2 and moisture in proportion, we have in this increase in temperature an almost ideal index of the quality of the air. A recording thermometer with a large dial face, hung or placed so as to be as readily seen as a clock, is the best known gauge of an occupied room.

If the air current through an occupied space is sufficient to carry away the increased moisture and to keep the temperature even, it will lower the carbon dioxide in the same proportion. This may be accepted as true without chemical examination (there are occasionally other sources of CO_2). The humidity is therefore an excellent indicator of the degree of ventilation, and a recording hygrometer is most desirable to place alongside the recording thermometer. Frequent observation and record may replace these rather expensive instruments to a degree.

We feel safe in stating that probably the best engineering practice

in ventilation today is in the use of these instruments, combined with training in the detection of odors. Only in cases of control or inspection will the determination of CO_2 be necessary when these instruments are at hand and when time for observing them is available. But there are frequent circumstances in which CO_2 is an equally good indicator and the tests for it more convenient of application, but they should partake of the rapidity and comparative accuracy of the instruments, and should not require the engineer to be burdened with cumbersome apparatus. For these purposes a sufficient degree of accuracy may be defined as within two-tenths to three-tenths of a part per 10,000, with a possible maximum error of five-tenths.

It does not seem to be possible in the present state of our knowledge to devise chemical tests for carbon dioxide which may be put with safety into the hands of unskilled persons, as may thermometers, but chemists and trained inspectors may use one of the following methods with confidence in their accuracy after a considerable practice, always using *outside air as a standardizing* medium. This will show at once any errors due to changing strength of the testing solution or fault in the manipulation.

The testing solution is not only carefully prepared, but protected against change while using by clamping the rubber stopper with a screw, or, in the case of additional bottles to be transported, by covering the stoppers with paraffin. The mounted automatic pipette ("Air, Water, and Food," page 42) is most convenient, but the inspector may mount an ordinary burette to answer the same purpose of delivering a measured 10 c.c. of solution.

The apparatus most used for this purpose in recent years is the Fitz or the Wolpert "shaker" ("Air, Water, and Food," page 43), a graduated glass tube in which successive small quantities of air are brought into contact for a definite time (thirty seconds) with a known volume of standard lime water, using the same solution for each partial sample of air, until the color of the indicator disappears. The relation between the quantity of CO_2 present and the total amount of air required to decolorize 6.3 c.c. of a standard saturated solution is shown in Table A.

TABLE A — FITZ SHAKER, PISTON, OR CYLINDER. 6.3 C.C. SATURATED LIME WATER PER LITER

Cubic centimeters of air.	Parts CO_2 in 10,000.
50	15.6
70	12.4
90	10.2
110	8.7
130	7.5
150	6.6
170	5.8
190	5.2
210	4.8
230	4.5
250	4.3
270	4.1
290	3.95
310	3.8
330	3.7
350	3.6

The taking of successive portions at even this short interval involves errors in sampling which in unskilled hands are liable to be serious. There is also an irregularity of action due to the fact that, as the solubility of a gas from a gaseous mixture is proportional to its partial pressure, the first portion of air gives up a larger part of its CO_2 than the later portions, in the same time; and therefore a much longer time should be allowed for absorption, which is not very practicable.

This property of gases is utilized, however, in another manner by the method of Cohen and Appleyard, in which the lapse of time is used to indicate the amount of CO_2 present in the mixture. This method, based as it is on a well-known scientific principle, has not received the attention it deserves; although it has been experimented with until it is, we think, on a workable basis.

The following methods of collecting the sample may be used according

to circumstances and may be described as (*a*) the water siphon; (*b*) the piston apparatus; (*c*) the steam-caused vacuum.

The alkaline solution is the same whatever method of collection is used and is made from a saturated solution of "lime water" of whatever strength is desired. 2.5, 5, and 10 c.c. to the liter are most available, according to the character of the air to be tested, the medium strength being of most general usefulness. Sodium or potassium carbonate, which readily takes on another molecule of carbon dioxide, may be substituted, whenever weighing out the pure solid is preferable to preparing the lime water. There may be also a slight increase in rapidity of action. These acid carbonate solutions keep better than caustic standards.

(*a*) *The Water Siphon Method.*—Two bottles (diameter one-third the height) of nearly equal capacity are fitted with rubber stoppers carrying small glass tubing, connected by several feet of rubber connector, with clamps (Fig. 1). One bottle is completely filled with water, nearly free from carbon dioxide.

The pair of bottles is taken to the place from which the air is to be collected. The inlet tube may be long to reach to near the ceiling, or short; if long, the first siphoning should be rejected, to secure filling the inlet tube with the air desired, the stoppers exchanged, and the sample taken. The air-filled bottle is stoppered and taken to the laboratory; or the test solution is at once added, the bottle stoppered and shaken, noting minutes and seconds. One bottle of water with a small reserve will serve for a number of takings before absorbing a deleterious amount of CO_2.

(*b*) *The Piston Method.*—In the piston method a glass cylinder containing approximately 600 c.c. is used. The two ends of the cylinder (Fig. 2) are of brass, one being pierced by a stopcock to admit the air to the tube, and the other by the connecting rod of the piston, which is made to fit the walls of the cylinder as closely as possible. The piston must be tight against the bottom of the cylinder. Then, with the apparatus at arm's length, the stopcock in the bottom is opened, and with a steady pull on the connecting rod the cylinder is filled with the desired air, care being taken to pull the piston tight against the upper end of the cylinder. After closing the stopcock the cylinder is ready to be taken to the laboratory for testing.

10 c.c. of lime water solution, colored by phenolphthalein, is run into the cylinder and the stopcock immediately closed. The tip of the burette, containing the 10 c.c. of lime water, is held at the lip of the stopcock

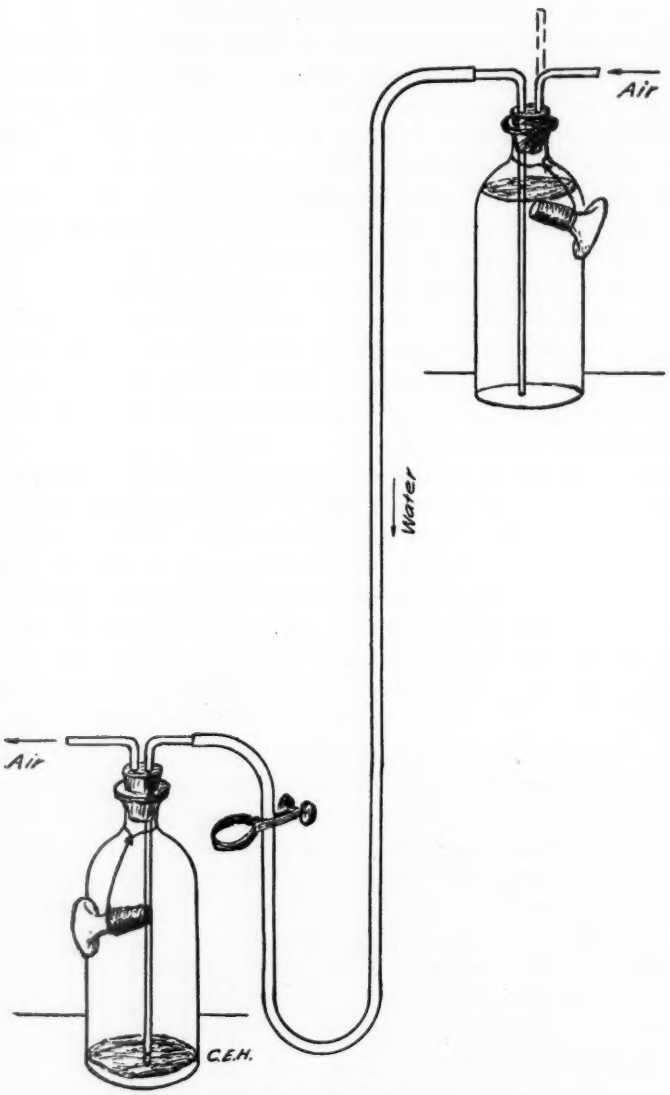

FIG. 1.— WATER-SIPHON APPARATUS

(made with a lip for the purpose), and the solution runs down the interior sides of the stopcock as the displaced air comes out of the centre. The number of seconds of gentle shaking before the color of the indicator disappears over white paper is recorded. This method may be used for samples taken by the siphon or vacuum methods, as well as the piston. From the known strength of the solution and the time, the number of parts of CO_2 per 10,000 may be read from the table.

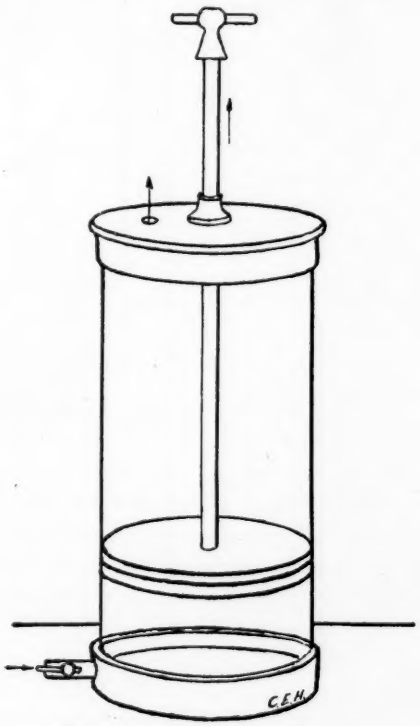

FIG. 2.—CYLINDER WITH PISTON

TABLE B—TIME METHOD. SAME SOLUTION AS IN TABLE A

TIME.		Parts CO_2 in 10,000.
Minutes.	Seconds.	
0	30	15.6
0	45	12.1
1	0	9.9
1	15	8.4
1	30	7.2
1	45	6.3
2	0	5.5
2	15	4.9
2	30	4.4
2	45	4.0
3	0	3.8
3	15	3.7
3	30	3.6

(*c*) *The Steam Vacuum Method.*—The steam is supplied by a 500 c.c. flask serving as a boiler, with a Tirrill burner to supply the heat. The flask (Fig. 3) is fitted with a rubber stopper carrying a No. 6 glass tube, bent so that one end extends within ½ inch of the bottom of the bottle when placed in position on the stand. The bottles used are of about 500 c.c. capacity, made for a ground-glass stopper but fitted with a rubber stopper.

To prepare the jet, the water in the flask is allowed to boil for five minutes in order to expel completely the air in the water and the flask. The pressure should be sufficient to throw the vaporized steam at least 1 foot above the exposed end of the tube.

The empty bottle is placed on the stand in an inverted position and allowed to remain for three minutes. In the meantime a thin coating of vaseline is applied half way up the sides of the stopper. The vaseline acts as an unguent, reducing the coefficient of friction to such an extent that the principal resistance is due to the reaction of the stopper against

compression. This enables one to force the stopper in far enough to bring the glass and rubber into intimate contact, which is essential. The vaseline also fills the interstices between the rubber and the glass, which makes leakage impossible.

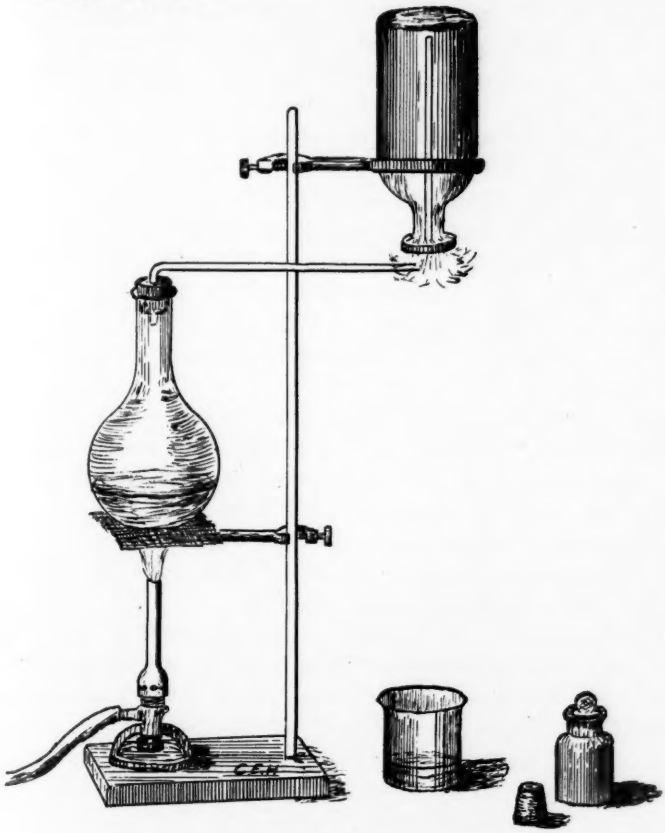

FIG. 3.— STEAM-VACUUM APPARATUS
From the thesis of Carl E. Hanson, 1908

Protecting the hand with a cloth, the bottle is raised from the stand, and the instant it clears the end of the tube the stopper is inserted while the bottle is still inverted. The stopper may be pushed in more securely by pushing it against the table with a few pounds' pressure while the bottle is still in the inverted position. The stopper is kept in under this pressure for a few minutes until the vacuum begins to form, after which the atmospheric pressure will keep it in place.

All the bottles required are treated in the same way. The rubber stoppers should be at least one size larger than would ordinarily be used for the bottles, and should project three-eighths of an inch or more to be easily removed when the sample is to be taken.

Sample bottles may be tested for completeness of vacuum by holding them in an inverted position under water at 70° F., free from carbon dioxide, and removing the stopper. After the water has replaced the vacuum, the stopper is inserted and the bottle removed.

Testing the Apparatus.—For the testing of the methods we have used the "live box," or air-tight room, devised in 1897 by Herbert E. Smith for his thesis on schoolhouse ventilation. Small weighed candles are placed in a flat-bottomed glass dish, lighted, the box closed and screwed tight, and the candles allowed to burn out. The electric fan is kept running to mix the air. After an hour samples may be drawn from the space at any of the three different levels desired, through glass tubes which the box carries. The following are examples of tests made in this manner.

Two candles three-eighths of an inch long and weighing six-tenths of a gram each were burned in a box containing 12 cubic feet of air. The candles burned for five minutes, and the resulting carbon dioxide content was from twenty to twenty-eight parts.

Two candles 2 inches long and together weighing 6.8 grams, burned in the large box (cubic contents 86.625 cubic feet) for forty-five minutes, produced an air containing thirty parts CO_2.

That the air in the box is uniformly charged with CO_2 (when the fan is running) and that it remains constant is shown by the following times of neutralization by the time method. These samples were taken at different times during the same day:

Trial.	Whole Solution.	Half Solution.
	Time.	Time.
	Seconds	Seconds
1	15	25
2	15	25
3	15	23
4	15	23
5	15	25

The outdoor air has too low a carbon dioxide content to serve for the test of an apparatus designed to detect larger quantities, and the air of well-ventilated rooms, as most of the schoolrooms are, is not only too good, but subject to too many variations to serve as reservoirs of constant air. The "box" has served us well in these respects, and with weighed candles repetition of the tests is easy. The air may remain constant for two weeks if only the small quantities are removed.

Interpretation of Results.—If in a crowded hall the temperature is less than 70° F., if the wet and dry bulb thermometers are 7° apart (less than 70 per cent. humidity), with no appreciable odor, and if the carbon dioxide is less than seven parts per 10,000, the air may be said to be satisfactory; but if the temperature is 80°, the wet and dry bulb only 4° apart (humidity 83 per cent.), and the carbon dioxide eight parts, with a close odor, then measures should be taken at once to remedy the condition.

The ideal condition for constant occupancy is: thermometer 68°, humidity 68 per cent., or wet and dry bulb 6° to 7° apart, with carbon dioxide less than six parts per 10,000 of air.

If these general results may be obtained, the smaller differences in readings may be discarded until the public is educated to this extent.

BOOK REVIEWS

Rocks and Rock Minerals[1]

Few if any petrologists are better qualified by reason of notable attainments in the science, as well as by long experience in teaching it, to write a manual of petrology than is Professor Pirsson, of Yale University, and it is with pleasure that we note the appearance of the book before us. Teachers of petrology will in general, we believe, fully agree with the author's opinion as expressed in his preface, that there has long been a need for a "small, concise, and practical treatise" on petrology in which the subject is dealt with entirely from a megascopic standpoint. Mining engineers and others who have to deal with rocks in a practical way have also felt the urgent need of such a book for purposes of reference. In our opinion the present manual meets this need in a highly satisfactory manner, and its publication marks a distinct advance in the treatment of elementary petrology. A general idea of the scope of the book may be obtained from the table of contents which follows:

Part I. *Introductory and General Considerations.*

Chapter I. Scope of Petrology: Historical Methods of Study.

Chapter II. Chemical Character of the Earth's Crust and Its Component Minerals.

Part II. *Rock Minerals.*

Chapter III. Important Properties of Minerals.

Chapter IV. Description of the Rock-making Minerals.

Chapter V. Determination of the Rock-making Minerals.

Part III. *The Rocks.*

Chapter VI. General Petrology of Igneous Rocks.

Chapter VII. Description of Igneous Rocks.

Chapter VIII. Origin and Classification of Stratified Rocks.

Chapter IX. Description of Stratified Rocks.

---

[1] Rocks and Rock Minerals. A Manual of the Elements of Petrology without the Use of the Microscope. By Louis V. Pirsson. New York: Wiley. London: Chapman. 414 pp., 74 il., 36 pls., 12mo.

Chapter X. Origin, General Characters, and Classification of the Metamorphic Rocks.

Chapter XI. Description of the Metamorphic Rocks.

Chapter XII. The Determination of Rocks.

Index.

The arrangement of the material in the various chapters is admirable throughout, while discussions, descriptions, and statements in general are accurate, clear, concise, yet sufficiently complete, and are written in a style which is attractive and easy to read. Chapter IV, dealing with the general petrology of the igneous rocks, seems particularly worthy of notice, since it presents such material of a general character, both practical and theoretical, as is really essential for a clear understanding of igneous rocks in a manner entirely in keeping with the most recent developments of the science, and yet within the comprehension of those not thoroughly trained in physical-chemistry, nor in microspetrology—a task that is not an easy one. An idea of the contents of this chapter will be gathered from the following topics, which are among those discussed therein: The modes of occurrence of igneous rocks; the chemical composition of magmas and their differentiation; the crystallization of silicate solutions (magmas) and the development of texture in igneous rocks; contact metamorphism; the classification of the igneous rocks.

In regard to the classification mentioned above, a system has been developed entirely consistent with megascopic petrology, all distinctions being based upon differences of texture or of mineral composition that can be made out by the careful study of good hand specimens with the aid of a pocket lens and a knife, in some few instances supplemented by a simple chemical test. The first division is made on the basis of differences of grain (granularity) into three classes. These are further divided according as the rock in question is porphyritic or non-porphyritic. Further division is made, chiefly upon differences of mineral composition, into a few broad groups which are designated by familiar rock names (granite, diorite, etc.) firmly fixed in petrological literature by long usage. The more important varieties falling under these various groups or kinds of rock, but which for microscopical or other reasons have received special names from petrographers, are referred to in appropriate places, so that the significance of such names when encountered can be easily found by reference to the book. Among the names adopted for the rock groups it may be noted that dolerite has been retained, very wisely it seems, to designate those granular, igneous rocks with predomi-

nant ferro-magnesian minerals, but in which it is not possible to tell positively just what ferro-magnesian mineral is present. This group will therefore include much that is commonly referred to as diabase. Felsite (or felsite-porphyry) is used for those nearly or entirely dense rocks, light in color, and generally highly feldspathic in character, while basalt (or basalt-porphyry) covers those dense, dark-colored, igneous rocks, for the most part ferro-magnesian in character. It will be noted that both of these terms, felsite and basalt, have been given a broader meaning than is customary in books covering a somewhat similar field. For example, dacites and most andesites fall under the head of felsite. Directions, however, for recognizing such varieties, when it is possible to do so microscopically, are given. The classification is summarized in a convenient table.

While some teachers will doubtless wish to make minor additions to the scheme of classification in their classroom work, the scheme as a whole appears so sane, simple, and practical that it can hardly fail to meet with general approval, and it is to be hoped that it will also come shortly into general use. In such an event it would be a strong influence toward uniformity and simplicity of practice among field workers in geology and petrology.

In Chapter VII we find the descriptions of individual kinds of rock treated under such appropriate headings as: Mineral Composition; General Properties; Chemical Composition (the latter illustrated by a few well-chosen analyses); Occurrence and Alteration. Thus while the descriptions furnish one with data useful for the recognition of the rock in the field or laboratory, they also furnish in a most satisfactory manner what might be termed the Natural History of the rock.

With so excellent a manual available as a basis for petrological study, it is to be hoped that it may be substituted for the dry and generally uninteresting lecturing so common in petrological laboratories, as well as for the too numerous laboratory guides and notes of inferior quality, and thus promote a general improvement in petrological teaching.

In conclusion it may be said that the book is conspicuous by reason of its typographical excellence and for the superior quality of the illustrations, which illustrate the text admirably.

CHARLES H. WARREN.

Massachusetts Institute of Technology, Boston, Mass.

Climate and Weather of Maryland[1]

Volume II of the Reports of the Maryland Weather Service appeared in June, 1908. This volume is devoted to a "Report on the Climate and Weather of Baltimore and Vicinity," by Dr. Oliver L. Fassig.

The report is divided into two portions, the first dealing with the climate of Baltimore, including atmospheric pressure, temperature of the atmosphere, humidity, precipitation, sunshine and cloudiness, the winds, and electrical phenomena.

The second portion, the weather of Baltimore, deals largely with storms. There is a general discussion of cyclones and anti-cyclones, weather charts of the Northern Hemisphere, and the principal climatic zones. This is followed by chapters on winter weather, including various types of storms and certain particular ones. The spring weather, the summer weather, and the autumn weather are discussed and illustrated in a similar way.

The final chapter of the book is an historical one on foretelling the weather.

This treatise is remarkably complete in all its details, and might serve as a text-book of meteorology. The value of the text is greatly enhanced by the numerous charts and graphic diagrams, besides many tables, giving data from 1876 to 1903.

---

[1] Maryland Weather Service. Vol. II. Baltimore: Johns Hopkins Press, 1907. 515 pp., il., pls.